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TEXTBOOKS ON PHYSICAL CHEMISTRY

EDITED BY SIR WILLIAM RAMSAY, K.C.B., D.Sc., F.R.S.

AND

F. G. DONNAN, C.B.E., M.A., PH.D., F.I.C., F.R.S.

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THE PHASE RULE

AND ITS APPLICATIONS

BY

ALEXANDER FINDLAY

M.A., D.Sc., F.I.C.

PROFESSOR OF CHEMISTRY, UNIVERSITY OF ABERDEEN

WITH 165 FIGURES

SIXTH EDITION

REVISED AND LARGELY RE-WRITTEN

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VOID

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TO

WILDER D. BANCROFT

PREFACE TO THE SIXTH EDITION

In order to make possible a more systematic treatment of the subject and a fuller and better-adjusted consideration of recent advances, it has been found advisable to make somewhat extensive alterations in the now twenty-three-year-old general framework of the book. These changes affect, more especially, those chapters which deal with equilibria in one and two component systems. These chapters have not only been revised, but have been re-cast, re-arranged, and, to a considerable extent, re-written. In these sections, the nature of the equilibria in intensively dried systems and the Smits theory of allotropy have also been discussed, although the limitations of space have necessitated brevity. Greater emphasis, also, has been laid on the applications of the Clausius-Clapeyron equation to the calculation of changes of equilibria with pressure and temperature.

Although it has not been considered necessary or advisable to subject the sections dealing with three and four component systems to any very drastic treatment, they have, nevertheless, been carefully revised and brought up to date. Moreover, a new chapter (Chapter XVI.) on the practical applications of equilibrium diagrams has been added. This chapter, it is hoped, will prove of interest and of value to the student, as affording illustrations of the practical applications of the Phase Rule to the study of three-component systems formed by water and two salts with a common ion, and as showing how the equilibrium (solubility) diagrams, constructed on the basis of experimental data, can be used to guide the practical operations of the winning of salts by crystallisation from solution. To make room for this new chapter and for the other additions made to various sections of the book, the chapter on the equilibria between iron, carbon monoxide, and carbon dioxide, which appeared in previous editions, has had to be sacrificed. The gain, it is hoped, will outweigh the loss.

A. F.

October, 1927.

PREFACE

Although we are indebted to the late Professor Willard Gibbs for the first enunciation of the Phase Rule, it was not till 1887 that its practical applicability to the study of Chemical Equilibria was made apparent. In that year Roozeboom disclosed the great generalisation, which for upwards of ten years had remained hidden and unknown save to a very few, by stripping from it the garb of abstract Mathematics in which it had been clothed by its first discoverer. The Phase Rule was thus made generally accessible ; and its adoption by Roozeboom as the basis of classification of the different cases of chemical equilibrium then known established its value, not only as a means of co-ordinating the large number of isolated cases of equilibrium and of giving a deeper insight into the relationships existing between the different systems, but also as a guide in the investigation of unknown systems.

While the revelation of the principle embedded in the Phase Rule is primarily due to Roozeboom, it should not be forgotten that, some years previously, van't Hoff, in ignorance of the work of Willard Gibbs, had enunciated his " law of the incompatibility of condensed systems," which in some respects coincides with the Phase Rule ; and it is only owing to the more general applicability of the latter that the very important generalisation of van't Hoff has been somewhat lost sight of.

The exposition of the Phase Rule and its applications given in the following pages has been made entirely non-mathematical, the desire having been to explain as clearly as possible the principles underlying the Phase Rule, and to illustrate their application to the classification and investigation of equilibria, by means of a number of cases actually studied. While it has been sought to make the treatment sufficiently elementary to be understood by the student just commencing the study of chemical equilibria, an attempt has been made to advance his knowledge to such a stage as to enable him to study with profit the larger works on the subject, and to follow with intelligence the course

of investigation in this department of Physical Chemistry. It is also hoped that the volume may be of use, not only to the student of Physical Chemistry, or of the other branches of that science, but also to the student of Metallurgy and of Geology, for whom an acquaintance with at least the principles of the Phase Rule is becoming increasingly important.

In writing the following account of the Phase Rule, it is scarcely necessary to say that I have been greatly indebted to the larger works on Chemical Equilibria by Ostwald (*Lehrbuch*) Roozeboom (*Die Heterogenen Gleichgewichte*), and Bancroft (*The Phase Rule*); and in the case of the first-named, to the inspiration also of personal teaching. My indebtedness to these and other authors I have indicated in the following pages.

In conclusion, I would express my thanks to Sir William Ramsay, whose guidance and counsel have been constantly at my disposal; and to my colleagues, Dr. T. Slater Price and Dr. A. McKenzie, for their friendly criticism and advice. To Messrs. J. N. Friend, M.Sc., and W. E. S. Turner, B.Sc., I am also indebted for their assistance in reading the proof-sheets.

A. F.

November, 1903.

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THE PHASE RULE

CHAPTER I.

INTRODUCTION.

General.—Before proceeding to the more systematic treatment of the Phase Rule, it may, perhaps, be not amiss to give first a brief forecast of the nature of the subject we are about to study, in order that we may gain some idea of what the Phase Rule is, of the kind of problem which it enables us to solve, and of the scope of its application.

It has long been known that if water is placed in a closed, exhausted space, vapour is given off and a certain pressure is created in the enclosing vessel. Thus, when water is placed in the Torricellian vacuum of the barometer, the mercury is depressed, and the amount of depression increases as the temperature is raised. But, although the pressure of the vapour increases as the temperature rises, its value at any given temperature is constant, no matter whether the amount of water present or the volume of the vapour is great or small; if the pressure on the vapour is altered while the temperature is maintained constant, either the water or the vapour will ultimately disappear; the former by evaporation, the latter by condensation. At any given temperature within certain limits, therefore, water and vapour can exist permanently in contact with each other—or, as it is said, be in equilibrium with each other—only when the pressure has a certain definite value. The same law of constancy of vapour pressure at a given temperature, quite irrespective of the volumes of liquid and vapour,[1] holds good also in the case of alcohol, ether, benzene, and other pure liquids. It is, therefore, not unnatural to ask the question, Does it hold good for all liquids? Is it valid, for example, in the case of solutions?

We can find the answer to these questions by studying the behaviour of a solution—say, a solution of common salt in water—when placed in the Torricellian vacuum. In this case, also, it is observed that the pressure of the vapour increases as the temperature is raised, but the pressure is no longer independent of the volume; as the volume increases, the pressure slowly diminishes. If, however, solid salt is present in contact with the solution, then the pressure again becomes constant at constant temperature, even when the volume of the vapour is altered. As we see, therefore, solutions do not behave in the same way as pure liquids.

[1] Except when the volume of the liquid becomes exceedingly small, in which case the surface tension exerts an influence on the vapour pressure.

Moreover, on lowering the temperature of water, a point is reached at which ice begins to separate out; and if heat be now added to the system or withdrawn from it, no change will take place in the temperature or vapour pressure of the latter until either the ice or the water has disappeared.[1] Ice, water, and vapour, therefore, can be in equilibrium with one another only at one definite temperature and one definite pressure.

In the case of a solution of common salt, however, we may have ice in contact with the solution at different temperatures and pressures. Further, it is possible to have a solution in equilibrium not only with anhydrous salt (NaCl), but also with the hydrated salt ($NaCl, 2H_2O$), as well as with ice, and the question, therefore, arises: Is it possible to state in a general manner the conditions under which such different systems can exist in equilibrium; or to obtain some insight into the relations which exist between pure liquids and solutions? As we shall learn, the Phase Rule enables us to give an answer to this question.

The preceding examples belong to the class of so-called "physical" equilibria, or equilibria depending on changes in the physical state. More than a hundred years ago, however, it was shown by Wenzel and Berthollet that "chemical" equilibria can also exist; that chemical reactions do not always take place completely in one direction as indicated by the usual chemical equation, but that before the reacting substances are all used up the reaction ceases, and there is a condition of equilibrium between the reacting substances and the products of reaction. As an example of this, there may be taken the process of lime-burning, which depends on the fact that when calcium carbonate is heated, carbon dioxide is given off and quicklime is produced. If, however, the carbonate is heated in a closed vessel, it will be found that it does not undergo complete decomposition. When the pressure of the carbon dioxide reaches a certain value (which is found to depend on the temperature), decomposition ceases, and calcium carbonate exists side by side with calcium oxide and carbon dioxide. Moreover, at any given temperature, the pressure of carbon dioxide is constant and independent of the amount of carbonate or oxide present, or of the volume of the gas; *nor does the addition of either of the products of dissociation, carbon dioxide or calcium oxide, cause any change in the equilibrium.* Here, then, we see that, although there are three different substances present, the equilibrium obeys the same law as the vapour pressure of a pure volatile liquid, such as water.

It might be supposed that this behaviour would be shown by other dissociating substances, *e.g.* ammonium chloride. When this substance is heated it dissociates into ammonia and hydrogen chloride, and at any given temperature the pressure of these gases is constant,[2] and is independent of the amounts of solid and gas present. So far, therefore, ammonium chloride behaves like calcium carbonate. If, however, one of the products of dissociation be added to the system,

[1] For reasons which will appear later (Chap. III.), the volume of the vapour is supposed to be large in comparison with that of the solid and liquid.

[2] Ramsay and Young, *Phil. Trans.*, 1886, 177, 87.

it is found that the pressure is no longer constant at a given temperature, but varies with the amount of gas, ammonia or hydrogen chloride, which is added. In the case of certain dissociating substances, therefore, addition of one of the products of dissociation alters the equilibrium, while in other cases it does not. With the help of the Phase Rule, however, a general interpretation of this difference of behaviour can be given—an interpretation which can be applied not only to the two cases cited, but to all cases of dissociation.

Again, it is well known that sulphur exists in two different crystalline forms, rhombic and monoclinic, each of which melts at a different temperature. The problem here is, therefore, more complicated than in the case of ice, for there is now a possibility not only of one solid form, but of two different forms of the same substance existing in contact with liquid. What are the conditions under which these two forms can exist in contact with liquid, either singly or together, and under what conditions can the two solid forms exist together without the presence of liquid sulphur? To these questions an answer can also be given with the help of the Phase Rule.

These cases are, however, comparatively simple; but when we come, for instance, to study the conditions under which solutions are formed, and especially when we inquire into the solubility relations of salts capable of forming, perhaps, a series of crystalline hydrates; and when we seek to determine the conditions under which these different forms can exist in contact with the solution, the problem becomes more complicated, and the need for some general guide to the elucidation of the behaviour of these different systems becomes more urgent.

It is, now, to the study of such physical and chemical equilibria as those above-mentioned that the Phase Rule finds application; to the study, also, of the conditions regulating, for example, the formation of alloys from mixtures of the fused metals, or of the various salts of the Stassfurt deposits; the behaviour of iron and carbon in the formation of steel and the separation of different minerals from a fused rock-mass. With the help of the Phase Rule we can group together into classes the large number of different isolated cases of systems in equilibrium; with its aid we are able to state, in a general manner at least, the conditions under which a system can be in equilibrium, and by its means we can gain some insight into the relations existing between different kinds of systems.

Homogeneous and Heterogeneous Equilibrium.—Before passing to the consideration of this generalisation, it will be well first to make mention of certain restrictions which must be placed on its treatment, and also of the limitations to which it is subject. If a system is uniform throughout its whole extent, and possesses in every part identical physical properties and chemical composition, it is said to be *homogeneous*. This term does not imply that a homogeneous system consists of only one atomic or molecular species, but rather that our methods of investigation do not allow us to detect in the system portions of matter of greater than atomic or molecular

dimensions. Thus, for example, a solution of sodium chloride in water is said to be homogeneous. An equilibrium occurring in such a homogeneous system (such as the equilibrium occurring in the formation of an ester in alcoholic solution) is called *homogeneous equilibrium*. If, however, the system consists of parts which have different physical properties, perhaps also different chemical properties, and which are marked off and separated from one another by bounding surfaces, the system is said to be *heterogeneous*. Such a system is formed by ice, water, and vapour, in which the three portions, each in itself homogeneous, can be mechanically separated from one another. When equilibrium exists between different, physically distinct parts, it is known as *heterogeneous equilibrium*. It is with heterogeneous equilibria, with the conditions under which a heterogeneous system can exist, that we shall deal here.

A certain degree of restriction must, however, be introduced, and we shall not take into account changes of equilibrium due to the action of electrical, magnetic, or capillary forces, or of gravity; but shall discuss only those which are due to changes of pressure, temperature, and volume (or concentration).

Real and Apparent Equilibrium.—In discussing equilibria, also, a distinction must be drawn between real and apparent equilibria. In the former case there is a state of rest which undergoes continuous change with change of the conditions (*e.g.* change of temperature or of pressure), and for which the chief criterion is that *the same condition of equilibrium is reached from whichever side it is approached*. Thus in the case of a solution, if the temperature is maintained constant, the same concentration will be obtained, no matter whether we start with an unsaturated solution to which we add more solid, or with a supersaturated solution from which we allow solid to crystallise out; or, in the case of water in contact with vapour, the same vapour pressure will be obtained. no matter whether we heat the water up to the given temperature or cool it down from a higher temperature. In this case, water and vapour are in *real* equilibrium. On the other hand, water in contact with hydrogen and oxygen at the ordinary temperature is a case only of *apparent* equilibrium; on changing the pressure and temperature continuously within certain limits there is no continuous change observed in the relative amounts of the two gases. On heating beyond these limits there is a sudden and not a continuous change, and the system no longer regains its former condition on being cooled to the ordinary temperature. In all such cases the system may be regarded, formally, at least, as undergoing change and as tending towards a state of true or real equilibrium, but with such slowness that no change is observed.

Although the case of water in contact with hydrogen and oxygen is an extreme one, it must be borne in mind that the condition of true equilibrium may not be reached instantaneously or even with measureable velocity, and in all cases it is necessary to be on one's guard against mistaking apparent (or false) for real (or true) equilibrium. The importance of this will be fully illustrated in the sequel.

CHAPTER II.

THE PHASE RULE.

ALTHOUGH the fact that chemical reactions do not take place completely in one direction, but proceed only to a certain point and there make a halt, was known in the last quarter of the eighteenth century (Wenzel, 1777; Berthollet, 1799); and although the opening and subsequent decades of the following century brought many further examples of such equilibria to our knowledge, it was not until the last quarter of the nineteenth century that a theorem, general in its application and with foundations weakened by no hypothetical assumptions as to the nature or constitution of matter, was put forward by Willard Gibbs;[1] a generalisation which serves at once as a golden rule by which the condition of equilibrium of a system can be tested, and as a guide to the similarities and dissimilarities existing in different systems.

Before that time, certainly, attempts had been made to bring the different known cases of equilibria—chemical and physical—under general laws. From the very first, both Wenzel[2] and Berthollet[3] recognised the influence exercised by the *mass* of the substances on the equilibrium of the system. It was reserved, however, for Guldberg and Waage, by their more general statement and mathematical treatment of the Law of Mass Action,[4] to inaugurate the period of quantitative study of equilibria. The law which these investigators enunciated served satisfactorily to summarise the conditions of equilibrium in many cases both of homogeneous and, with the help of certain assumptions and additions, of heterogeneous equilibrium. By reason, however, of the fact that it was developed on the basis of the kinetic and molecular theories, and involved, therefore, certain assumptions as to the nature and condition of the substances taking part in the equilibrium, the law of mass action failed, as it necessarily must, when applied to those systems in which neither the number of different molecular aggregates nor the degree of their molecular complexity was known.

Ten years after the law of mass action was propounded by Guldberg and Waage, Willard Gibbs,[5] Professor of Physics in Yale University,

[1] *Trans. Connecticut Acad.*, 1874-1878; *Scientific Papers* (Longmans).
[2] Lehre von der chemischen Verwandtschaft der Körper, 1777.
[3] See Ostwald's *Klassiker*, No. 74.
[4] Etudes sur les affinités chimiques, 1867; Ostwald's *Klassiker*, No. 104.
[5] Died April, 1903.

showed how, in a perfectly general manner, free from all hypothetical assumptions as to the molecular condition of the participating substances, all cases of equilibrium could be surveyed and grouped into classes, and how similarities in the behaviour of apparently different kinds of systems, and differences in apparently similar systems, could be explained.

As the basis of his theory of equilibria, Gibbs adopted the laws of thermodynamics,[1] a method of treatment which had first been employed by Horstmann.[2] In deducing the law of equilibrium, Gibbs regarded a system as possessing only three independently variable factors [3]—temperature, pressure, and the concentration of the components of the system—and he enunciated the general theorem now usually known as the *Phase Rule*, by which he defined the conditions of equilibrium as a relationship between the number of what are called the phases and the components of the system.

Phases.—We have already seen (p. 4) that a heterogeneous system is made up of different portions, each in itself homogeneous but marked off in space and separated from the other portions by bounding surfaces. These homogeneous, physically distinct and mechanically separable portions are called *phases*. Thus ice, water, and vapour are three phases of the same chemical substance—water. A phase, however, whilst it must be physically and chemically homogeneous, need not necessarily be chemically simple. Thus, a gaseous mixture or a solution may form a phase; but a heterogeneous mixture of solid substances comprises as many phases as there are substances present. Thus when calcium carbonate dissociates under the influence of heat, calcium oxide and carbon dioxide are formed. There are then *two* solid phases present, viz. calcium carbonate and oxide, and one gas phase, carbon dioxide.

The *number of phases* which can exist side by side may vary greatly in different systems. In all cases, however, there can be but one gas or vapour phase on account of the fact that gases are miscible with one another in all proportions. In the case of liquid and solid phases, the number is indefinite, since the property of complete miscibility does not apply to them. The number of phases which can be formed by any given substance or group of substances also differs greatly, and in general increases with the number of participating substances. Even in the case of a single substance the number may be considerable; in the case of sulphur, for example, at least eight different solid phases are known (*v.* Chap. IV.).

It is of importance to bear in mind that equilibrium is *independent of the amounts* of the phases present.[4] Thus it is a familiar fact that

[1] For a mathematical treatment of the Phase Rule the reader is referred to Lewis, *A System of Physical Chemistry*, Vol. II. (Longmans).

[2] Liebig's *Annalen*, 1873, **170**, 192.

[3] The action of gravity and other forces being excluded (see p. 4).

[4] It may seem as if this were a contradiction of what was said on page 3 as to the effect of the addition of ammonia or hydrogen chloride to the system constituted by solid ammonium chloride in contact with its products of dissociation. There is,

the pressure of a vapour in contact with a liquid (*i.e.* the pressure of the saturated vapour) is unaffected by the amounts, whether relative or absolute, of the liquid and vapour ; also, the amount of a substance dissolved by a liquid is independent of the amount of solid in contact with the solution. It is true that deviations from this general law occur when the amount of liquid or the size of the solid particles is reduced beyond a certain point,[1] owing to the influence of surface energy ; but we have already (p. 4) excluded such cases from consideration.

Components.—Although the conception of phases is one which is readily understood, somewhat greater difficulty is experienced when we come to consider what is meant by the term *component ;* for the components of a system are not synonymous with the chemical elements or compounds present, *i.e.* with the *constituents* of the system, although both elements and compounds may be components. By the latter term there are meant only those constituents the concentration of which can undergo *independent* variation in the different phases, and it is only with these that we are concerned here.[2]

To understand the meaning of this term we shall consider briefly some cases with which the reader will be familiar, and at the outset it must be emphasised that the Phase Rule is concerned merely with those constituents which take part in the state of real equilibrium (p. 4) ; for it is only to the final state, not to the processes by which that state is reached, that the Phase Rule applies.

Consider now the case of the system water—vapour, or ice—water—vapour. The number of constituents taking part in the equilibrium here is only one, viz. the chemical substance, water. Hydrogen and oxygen, the constituents of water, are not to be regarded as components, because, in the first place, they are not present in the system in a state of real equilibrium (p. 4) ; in the second place, they are combined in definite proportions to form water, and their amounts, therefore, cannot be varied independently. A variation in the amount of hydrogen necessitates a definite variation in the amount of oxygen.

however, no contradiction, because in the case of ammonium chloride the gaseous phase consists of ammonia and hydrogen chloride in equal proportions, and in adding ammonia or hydrogen chloride alone we are not adding the gaseous phase, but only a constituent of it. Addition of ammonia and hydrogen chloride together in the proportions in which they are combined to form ammonium chloride would cause no change in the equilibrium.

[1] The vapour pressure of water in small drops is greater than that of water in mass, and the solubility of a solid is greater when in a state of fine subdivision than when in large pieces (*cf.* Hulett, *Z. physikal. Chem.*, 1901, **37**, 385). The vapour pressure of small crystals is also greater than that of large ones (Pawloff, *Z. physikal. Chem.*, 1909, **68**, 316).

[2] See Roozeboom, *Z. physikal. Chem.*, 1894, **15**, 150 ; *Heterogene Gleichgewichte*, I., p. 16 ; Wegscheider, *Z. physikal. Chem.*, 1903, **43**, 89 ; 1903, **45**, 496 ; *Z. anorgan. Chem.*, 1927, **159**, 161. Another statement of the Phase Rule in which the term component is replaced by the term "individual" and in which a factor occurs indicating the "number of independent restrictions on fixed conditions which are determined by the circumstances of the case but not included in the definition of the individuals" has been given by T. W. Richards (*Chem. News*, 1916, **114**, 37 ; *J. Amer. Chem. Soc.*, 1916, **38**, 983).

In the case, already referred to, in which hydrogen and oxygen are present along with water at the ordinary temperature, we are not dealing with a condition of true equilibrium. If, however, the temperature is raised to a certain point, a state of true equilibrium between hydrogen, oxygen, and water vapour will be possible. In this case hydrogen and oxygen will be components, because now they do take part in the equilibrium ; also, they need no longer be present in definite proportions, but excess of one or the other may be added. Of course, if the restriction be arbitrarily made that the free hydrogen and oxygen shall be present always and only in the proportions in which they are combined to form water, there will be, as before, only one component, water. From this, then, we see that a change in the conditions of the experiment (in the present case a rise of temperature) may necessitate a change in the number of the components.

It is, however, only in the case of systems of more than one component that any difficulty will be found ; for only in this case will a choice of components be possible. Take, for example, the dissociation of calcium carbonate into calcium oxide and carbon dioxide. At each temperature, as we have seen, there is a definite state of equilibrium. When equilibrium has been established, there are three different substances present—calcium carbonate, calcium oxide, and carbon dioxide ; and these are the constituents of the system between which equilibrium exists. Although these constituents take part in the equilibrium, they are not all to be regarded as components, for they are not mutually independent. On the contrary, the different phases are related to one another, and if *two* of these are taken, the composition of the third is defined by the equation

$$CaCO_3 = CaO + CO_2.$$

In deciding the number of components in any given system, not only must the constituents chosen be capable of independent variation, but a further restriction is imposed, and we obtain the following rule : *As the components of a system there are to be chosen the* SMALLEST NUMBER *of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*

Applying this rule to the case under consideration, we see that of the three constituents present when the system is in a state of equilibrium, only two are independently variable. It will further be seen that in order to express the composition of each phase present, two of these constituents are necessary. The system is, therefore, one of *two components*, or a system of the second order.

When we proceed to the actual choice of components, it is evident that any two of the constituents can be selected. Thus, if we choose as components $CaCO_3$ and CaO, the composition of each phase can be expressed by the following equations :—

$$CaCO_3 = CaCO_3 + o\,CaO$$
$$CaO = CaO + o\,CaCO_3$$
$$CO_2 = CaCO_3 - CaO$$

As we see, then, both zero and negative quantities of the components have been introduced; and similar expressions would be obtained if $CaCO_3$ and CO_2 were chosen as components. The matter can, however, be simplified and the use of negative quantities avoided if CaO and CO_2 are chosen; and it is, therefore, customary to select these as the components.

While it is possible in the case of systems of the second order to choose the two components in such a way that the composition of each phase can be expressed by positive quantities of these, such a choice is not always possible when dealing with systems of a higher order (containing three or four components).

From the example which has just been discussed, it might appear as if the choice of the components was rather arbitrary. On examining the point, however, it will be seen that the arbitrariness affects only the *nature*, not the *number*, of the components; a choice could be made with respect to which, not to how many, constituents were to be regarded as components. As we shall see presently, however, it is only the number, not the nature of the components, that is of importance.

After the discussion of the conditions which the substances chosen as components must satisfy, another method may be given by which the number of components present in a system can be determined. Suppose a system consisting of several phases in equilibrium, and the composition of each phase determined by analysis. If each phase present, regarded as a whole, has the same composition, the system contains only one component, or is of the first order. If two phases must be mixed in suitable quantities in order that the composition of a third phase may be obtained, the system is one of two components or of the second order; and if three phases are necessary to give the composition of a fourth co-existing phase, the system is one of three components, or of the third order.[1]

Although the examples to be considered in the sequel will afford sufficient illustration of the application of the rules given above, one case may perhaps be discussed to show the application of the method just given for determining the number of components.

Consider the system consisting of Glauber's salt in equilibrium with solution and vapour. If these three phases are analysed, the composition of the solid will be expressed by Na_2SO_4, $10H_2O$; that of the solution by $Na_2SO_4 + xH_2O$, while the vapour phase will be H_2O. The system evidently cannot be a one-component system, for the phases have not all the same composition. By varying the amounts of two phases, however (*e.g.* Na_2SO_4, $10H_2O$ and H_2O), the composition of the third phase—the solution—can be obtained. The system is, therefore, one of *two components*.

But sodium sulphate can also exist in the anhydrous form and as the hydrate Na_2SO_4, $7H_2O$. In these cases there may be chosen as

[1] Ostwald, *Lehrbuch*, II., **2**, 478.

components Na_2SO_4 and H_2O, and Na_2SO_4, $7H_2O$ and H_2O respectively. In both cases, therefore, there are *two components*. The two systems (Na_2SO_4, $10H_2O$—H_2O, and Na_2SO_4, $7H_2O$—H_2O) can, however, be regarded as special cases of the system Na_2SO_4—H_2O, and these two components will apply to all systems made up of sodium sulphate and water, no matter whether the solid phase is anhydrous salt or one of the hydrates. In all three cases, of course, the *number* of components is the same; but by choosing Na_2SO_4 and H_2O as components, the possible occurrence of negative quantities of components in expressing the composition of the phases is avoided; and, further, these components apply over a much larger range of experimental conditions. Again, therefore, we see that, although the number of the components of a system is definite, a certain amount of liberty is allowed in the choice of the substances; and we also see that the choice will be influenced by the conditions of experiment.

Summing up, now, we may say:—

(1) The components are to be chosen from among the constituents which are present when the system is in a state of true equilibrium, and which take part in that equilibrium.

(2) As components are to be chosen the *smallest number* of such constituents necessary to express the composition of each phase participating in the equilibrium, zero and negative quantities of the components being permissible.

(3) In any given system the *number* of the components is definite, but may alter with alteration of the conditions of experiment. A certain freedom of choice, however, is allowed in the (qualitative, not quantitative) selection of the components, the choice being influenced by considerations of simplicity, suitability, or generality of application.[1]

Degree of Freedom. Variability of a System.—It is well known that in dealing with a certain mass of gas or vapour, *e.g.* water vapour, if only one of the independently variable factors—temperature, pressure, and concentration (or volume)—is fixed, the state of the gas or vapour is undefined; while occupying the same volume (the concentration, therefore, remaining unchanged), the temperature and the pressure may be altered; at a given temperature, a gas can exist under different pressures and occupy different volumes, and under any given pressure the temperature and volume may vary. If, however, two of the factors are arbitrarily fixed, then the third factor can only have a certain definite value; at any given values of temperature and pressure a given mass of gas can occupy only a definite volume.

Suppose, however, that the system consists of water in contact with vapour. The condition of the system then becomes perfectly defined on arbitrarily giving one of the variables a certain value. If the temperature is fixed, the pressure under which water and water vapour can coexist is also determined; and conversely, if a definite pressure is chosen, the temperature is also defined. Water and vapour can coexist under a given pressure only at a definite temperature.

[1] See also Hoitsema, *Z. physikal. Chem.*, 1895, **17**, 651.

Finally, let the water and vapour be cooled down until ice begins to separate out. So soon as the third phase, ice, appears, the state of the system as regards temperature and pressure of the vapour is perfectly defined, and none of the variables can be arbitrarily changed without causing the disappearance of one of the phases—ice, water, or vapour.

We see, therefore, that in the case of some systems two, in other cases, only one of the independent variables (temperature, pressure, concentration) can be altered without destroying the nature of the system; while in other systems, again, these variables have all fixed and definite values. We shall therefore define the number of degrees of freedom [1] of a system as the *number of the variable factors, temperature, pressure, and concentration of the components, which must be arbitrarily fixed in order that the condition of the system may be perfectly defined.* From what has been said, therefore, we shall describe a gas or vapour as having two degrees of freedom; the system water—vapour as having only one; and the system ice—water—vapour as having no degrees of freedom. We may also speak of the *variability* or *variance* of a system, and describe a system as being invariant, univariant, bivariant, multivariant,[2] according as the number of degrees of freedom is nought, one, two, or more than two.

A knowledge of its variability is, therefore, of essential importance in studying the condition and behaviour of a system, and it is the great merit of the Phase Rule that *the state of a system is defined entirely by the relation existing between the number of the components and the phases present*, no account being taken of the molecular complexity of the participating substances, nor any assumption made with regard to the constitution of matter. It is, further, as we see, quite immaterial whether we are dealing with "physical" or "chemical" equilibrium; in principle, indeed, no distinction need be drawn between the two classes, although it is nevertheless often convenient to make use of the terms, in spite of a certain amount of indefiniteness which attaches to them—an indefiniteness, indeed, which attaches equally to the terms "physical" and "chemical" process.

The Phase Rule.—The Phase Rule of Gibbs, which defines the condition of equilibrium by the relation between the number of coexisting phases and components, may be stated as follows: A system consisting of n components can exist in $n + 2$ phases only when the temperature, pressure, and concentration have fixed and definite values; if there are n components in $n + 1$ phases, equilibrium can exist while one of the factors varies, and if there are only n phases, two of the varying factors may be arbitrarily fixed. This rule, the application of which, it is hoped, will become clear in the

[1] The term "degree of freedom" employed here must not be confused with the same term used to denote the various movements of a gas molecule according to the kinetic theory.

[2] Trevor, *J. Physical Chem.*, 1902, **6**, 136.

sequel, may be very concisely and conveniently summarised in the form of the equation

$$F = n - r + 2 \quad \text{or} \quad F = n + 2 - r$$

where F denotes the variability or degrees of freedom of the system, n the number of the components, and r the number of phases. From the equations it can readily be seen that the greater the number of the phases, the fewer are the degrees of freedom. With increase in the number of the phases, therefore, the condition of the system becomes more and more defined, or less and less variable.

Classification of Systems according to the Phase Rule.—We have already learned in the introductory chapter that systems which are apparently quite different in character may behave in a very similar manner. Thus it was stated that the laws which govern the equilibrium between water and its vapour are quite analogous to those which are obeyed by the dissociation of calcium carbonate into carbon dioxide and calcium oxide; in each case a certain temperature is associated with a definite pressure, no matter what the relative or absolute amounts of the respective substances may be. And other examples were given of systems which were apparently similar in character, but which nevertheless behaved in a different manner. The relations between the various systems, however, become perfectly clear and intelligible in the light of the Phase Rule. In the case first mentioned, that of water in equilibrium with its vapour, we have one component—water—present in two phases, *i.e.* in two physically distinct forms, viz. liquid and vapour. According to the Phase Rule, therefore, since $n = 1$ and $r = 2$, the degree of freedom F is equal to $1 + 2 - 2 = 1$; the system possesses one degree of freedom, as has already been stated. But in the case of the second system mentioned above there are two components, viz. calcium oxide and carbon dioxide (p. 9), and three phases, viz. two solid phases, CaO and $CaCO_3$, and the gaseous phase, CO_2. The number of degrees of freedom of the system, therefore, is $2 + 2 - 3 = 1$; this system, therefore, also possesses one degree of freedom. We can now understand why these two systems behave in a similar manner; both are univariant or possess only one degree of freedom. We shall therefore expect a similar behaviour in the case of all univariant systems, no matter how dissimilar the systems may outwardly appear. Similarly, all bivariant systems will exhibit analogous behaviour; and generally, systems possessing the same degree of freedom will show a like behaviour. In accordance with the Phase Rule, therefore, we may classify the different systems which may be found into invariant, univariant, bivariant, multivariant, according to the relation which obtains between the number of the components and the number of coexisting phases; and we shall expect that in each case the members of any particular group will exhibit a uniform behaviour. By this means we are enabled to obtain an insight into the general behaviour of any system, so soon as we have determined the number of the components and the number

of the coexisting phases. Moreover, knowing the number of components and the degree of freedom of a system, one can determine the number of coexisting phases. In this way it is possible to decide whether a given body is a single homogeneous substance (a single phase) or is a heterogeneous mixture.[1]

The adoption of the Phase Rule for the purposes of classification has been of great importance in studying changes in the equilibrium existing between different substances; for not only does it render possible the grouping together of a large number of isolated phenomena, but the guidance it affords has led to the discovery of new substances, has given the clue to the conditions under which these substances can exist, and has led to the recognition of otherwise unobserved resemblances existing between different systems.

Deduction of the Phase Rule.—In the preceding pages we have restricted ourselves to the statement of the Phase Rule, without giving any indication of how it has been deduced. At the close of this chapter, therefore, the mathematical deduction of the generalisation will be given, but in brief outline only, the reader being referred to works on Thermodynamics for a fuller treatment of the subject.[2]

All forms of energy can be resolved into two factors, the *capacity* factor and the *intensity* factor; but for the production of equilibrium, only the intensity factor is of importance. Thus, if two bodies having the same temperature are brought in contact with each other, they will be in equilibrium as regards heat energy, no matter what may be the amounts of heat (capacity factor) contained in either, because the intensity factor—the temperature—is the same. But if the temperature of the two bodies is different, *i.e.* if the intensity factor of heat energy is different, the two bodies will no longer be in equilibrium; heat will pass from the hotter to the colder until both have the same temperature.

As with heat energy, so with chemical energy. If we have a substance existing in two different states, or in two different phases of a system, equilibrium can occur only when the intensity factor of chemical energy is the same. This intensity factor may be called the *chemical potential;* and we can therefore say that a system will be in equilibrium when the chemical potential of each component is the same in all the phases in which the component occurs. Thus, for example, ice, water, and vapour have, at the triple point, the same chemical potential.

The potential of a component in any phase depends not only on the composition of the phase, but also on the temperature and the pressure (or volume). If, therefore, we have a system of n components existing in r phases, then, in order to fix the composition of unit mass of each phase, it is necessary to know the masses of $(n - 1)$ components

[1] For an application of this principle, see Wegelius, *Z. physikal. Chem.*, 1911, **77**, 587.

[2] See Lewis, *A System of Physical Chemistry*, Vol. II. (Longmans); Le Chatelier, *Compt. rend.*, 1920, **171**, 1033; Viola, *Atti. R. Accad. Lincei*, 1916, **25**, II. 245; Muller, *Compt. rend.*, 1908, **146**, 866.

in each of the phases. As regards the composition, therefore, each phase possesses $(n - 1)$ variables. Since there are r phases, it follows that, as regards composition, the whole system possesses $r(n - 1)$ variables. Besides these there are, however, two other variables, viz. temperature and pressure, so that altogether a system of n components in r phases possesses $r(n - 1) + 2$ variables.

In order to define the state of the system completely, it will be necessary to have as many equations as there are variables. If, therefore, there are fewer equations than there are variables, then, according to the deficiency in the number of the equations, one or more of the variables will have an undefined value; and values must be assigned to these variables before the system is entirely defined. The number of these undefined values gives us the variability or the degree of freedom of the system.

The equations by which the system is to be defined are obtained from the relationship between the potential of a component and the composition of the phase, the temperature and the pressure. Further, as has already been stated, equilibrium occurs when the potential of each component is the same in the different phases in which it is present. If, therefore, we choose as standard one of the phases in which all the components occur, then in any other phase in equilibrium with it, the potential of each component must be the same as in the standard phase. For each phase in equilibrium with the standard phase, therefore, there will be a definite equation of state for each component in the phase; so that, if there are r phases, we obtain for each component $(r - 1)$ equations; and for n components, therefore, we obtain $n(r - 1)$ equations.

But we have seen above that there are $r(n - 1) + 2$ variables, and as we have only $n(r - 1)$ equations, there must be

$$r(n - 1) + 2 - n(r - 1) = n + 2 - r$$

variables undefined. That is to say, the degree of freedom (F) of a system consisting of n components in r phases is

$$F = n + 2 - r.$$

CHAPTER III.

SYSTEMS OF ONE COMPONENT.

Although it is possible to state, in the form of a mathematical equation, the conditions of equilibrium in different systems, the understanding and practical application of the Phase Rule are simplified and facilitated by graphic representation. From the expression $F = n + 2 - r$, it follows that when one component exists in only one phase, the degree of freedom is 2 ; and this must be the maximum degree of freedom possible. All systems of one component can, therefore, be perfectly defined by giving values to, at most, two variable factors ; and the equilibrium conditions can be most conveniently represented graphically by a system of rectangular co-ordinates, the axes of which are pressure and temperature (pt-diagram). In such a diagram, invariant systems will be represented by points, univariant systems by lines, and bivariant systems by areas.

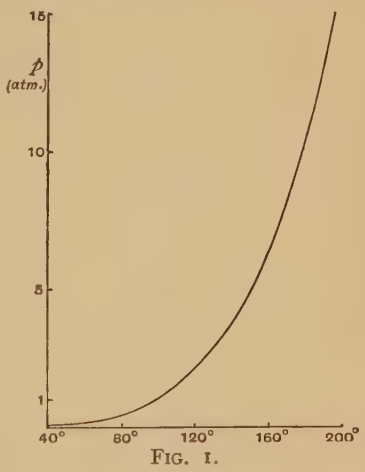

Fig. 1.

Univariant Systems.

Univariant systems are formed when one component exists in two phases. A single substance can, so far as is known, form only one gas phase and one liquid phase, but it may exist in more than one crystalline solid phase.[1] Since any pair of phases will constitute a univariant system, the number of such systems may vary greatly, and can be determined only by experiment.

Equilibrium between Liquid and Vapour. Vaporisation Curve. —A volatile liquid in equilibrium with its vapour constitutes a

[1] The term "solid" is not in itself sufficient to characterise a phase different from gas or liquid. An amorphous solid, glass, is merely a liquid cooled to such a low temperature that its viscosity becomes very great. The passage of an amorphous solid into liquid is a gradual and continuous one. In a crystalline solid, however, the atoms or molecules are arranged in a definite space lattice, and transition from a crystalline to a liquid phase is abrupt and definite.

univariant system, and the state of the system will be defined if one of the variable factors, pressure or temperature, be arbitrarily fixed. At a given temperature the pressure of the vapour will have a definite value; or, if a certain vapour pressure is maintained, coexistence of liquid and vapour will be possible only at a certain definite temperature. Each temperature, therefore, will correspond to a definite pressure; and if in the *pt*-diagram we join by a continuous line all the points indicating the values of the pressure corresponding to the different temperatures, we shall obtain a curve (Fig. 1) representing the variation of the vapour pressure with the temperature. This is the curve of vapour pressure, or the *vaporisation curve.*

The results of experiment are in complete harmony with the requirements of the Phase Rule, as is shown, for example, by the determinations of the vapour pressure of water carried out by Magnus,[1] Regnault,[2] Battelli,[3] Ramsay and Young,[4] Juhlin,[5] Thiesen and Scheel,[6] Holborn and Henning,[7] Holborn and Baumann,[8] Scheel and Heuse,[9] and others.

Some of the values of the vapour pressure of water at different temperatures are given in the following table,[10] and represented in Fig. 1 :—

VAPOUR PRESSURE OF WATER.

Temperature.	Pressure in cm. of mercury.	Temperature.	Pressure in cm. of mercury.
− 10°	0·2144	120°	148·9
0°	0·4579	130°	202·6
+ 20°	1·7539	150°	356·9
40°	5·534	200°	1164·7
60°	14·946	250°	2977·1
80°	35·547	270°	4118·6
100°	76·00	300°	6429·0
		374° (critical temperature)	16494·0 (217·5 atm.) (critical pressure)

The vapour pressure of a liquid is, of course, independent of the relative or absolute volumes of the liquid and vapour; [11] on increasing the volume at constant temperature, a certain amount of the liquid will pass into vapour, and the pressure will regain its former value. If, however, the pressure be permanently maintained at a value different from that corresponding to the temperature employed, then either

[1] *Pogg. Annalen*, 1844, **61**, 225. [2] *Mémoires de l'Acad.*, 1847, **21**, 405.
[3] *Annales chim. et phys.*, 1892 [6], **26**, 410; 1894 [7], **3**, 408.
[4] *Phil. Trans.*, 1884, **175**, 461; 1892, A, **183**, 107.
[5] *Bihang Svenska Akad. Handl.*, 1891, **17**, I. 1.
[6] *Abhandl. physikal.-tech. Reichsanstalt*, 1900, **3**, 71.
[7] *Annalen der Physik*, 1908 [4], **26**, 833.
[8] *Ibid.*, 1910 [4], **31**, 945. [9] *Ibid.*, 1909 [4], **29**, 723; 1910, **31**, 715.
[10] See also Henning, *Annalen der Physik*, 1907 [4], **22**, 609.
[11] See footnote 1, p. 7.

all the liquid will pass into vapour, or all the vapour will pass into liquid, and we shall have either vapour alone or liquid alone.

As the result of a large number of determinations, it has been found that all vapour-pressure curves have the same general form as that shown in Fig. 1, the curve being convex towards the temperature axis in the ordinary *pt*-diagram.

The interpolation and extrapolation of vapour-pressure curves is rendered very easy by means of a relationship which Ramsay and Young [1] found to exist between the vapour-pressure curves of different substances. It was observed that in the case of closely related substances, the ratio of the absolute temperatures corresponding to equal vapour pressures is constant, *i.e.* $\frac{T_1}{T'_1} = \frac{T_2}{T'_2}$. When the two substances are not closely related, it was found that the relationship could be expressed by the equation $\frac{T_1}{T'_1} = \frac{T_2}{T'_2} + c(t' - t)$ where c is a constant having a small positive or negative value, and t' and t are the temperatures at which one of the substances has the two values of the vapour pressure in question. By means of this equation, if the vapour-pressure curve of one substance is known, the vapour-pressure curve of any other substance can be calculated from the values at any two temperatures of the vapour pressure of that substance.

Upper Limit of Vaporisation Curve.—On continuing to add heat to a liquid contained in a closed vessel, the pressure of the vapour will continuously increase. Since with increase of pressure the density of the vapour must increase, and since with rise of temperature the density of the liquid must decrease, a point will be reached at which the densities of liquid and vapour become identical; the system ceases to be heterogeneous, and passes into one homogeneous phase. The temperature at which this occurs is called the *critical temperature*. To this temperature there will, of course, correspond a certain definite pressure, called the *critical pressure*. The curve representing the equilibrium between liquid and vapour must, therefore, end abruptly at the critical point.[2] At temperatures above this point no pressure, however great, can cause the formation of the liquid phase; at temperatures above the critical point the vapour becomes a gas. In the case of water, the critical temperature is 374°, and the critical pressure 217·5 atm.; at the point representing these conditions the vapour-pressure curve of water must end. The lower limit of the curve is determined by the range of the metastable state of the super-cooled liquid.

Theorems of van't Hoff and of Le Chatelier.—While the

[1] *Phil. Mag.*, 1886, **21**, 33. See also S. A. Moss, *Physical Rev.*, 1903, **16**, 356.

[2] Although in the system liquid—vapour, the liquid ceases to exist at the critical point, Tammann has found that the fusion curve (solid in contact with liquid) of phosphonium chloride can be followed up to temperatures above the critical point (*Arch. Néerland.*, 1901 [2], **6**, 244). See also Bridgman, *Physical Rev.*, 1914 [2], **3**, 126, 153.

Phase Rule gives, quite definitely, the conditions of equilibrium in any given heterogeneous system, it gives no information regarding changes of equilibrium brought about by alteration of the external conditions of temperature and pressure. For all such changes there exist two theorems, based on the laws of thermodynamics, by means of which the alterations in a system can be qualitatively predicted. The first of these, usually known as van't Hoff's *law of movable or mobile equilibrium*,[1] states: When the temperature of a system in equilibrium is raised, a reaction takes place within the system which is accompanied by absorption of heat; and, conversely, when the temperature is lowered, a reaction occurs which is accompanied by evolution of heat.

The second of the two theorems refers to the effect of change of pressure, and states: [2] When the pressure on a system in equilibrium is increased, a reaction takes place which is accompanied by a diminution of volume; and when the pressure is diminished, a reaction ensues which is accompanied by an increase of volume.

The demonstration of the universal applicability of these two theorems is due chiefly to Le Chatelier, who showed that they may be regarded as consequences of the general law of action and reaction. For this reason they are generally regarded as special cases of the more general law, known as the *theorem of Le Chatelier*,[3] which may be stated in the words of Ostwald, as follows: [4] *If a system in equilibrium is subjected to a constraint by which the equilibrium is altered, a reaction takes place which opposes the constraint*, i.e. *one by which its effect is partially annulled.*

This theorem of Le Chatelier is of very great importance, for it applies to all systems and changes of the condition of equilibrium,[5] whether physical or chemical; to vaporisation and fusion, to solution and chemical action. In all cases, whenever changes in the external condition of a system in equilibrium are produced, processes also occur within the system which tend to counteract the effect of the external changes.

By the introduction of the theorem of Le Chatelier the scope and practical utility of the Phase Rule are very greatly increased.

To illustrate the application of the theorem of Le Chatelier, let us consider the changes which take place in the system liquid—vapour. If the volume is kept constant, addition of heat will cause that reaction or process to take place which is accompanied by absorption of heat. Since vaporisation is accompanied by absorption of heat, liquid will pass into vapour, and the pressure will increase. The vapour pressure increases with rise of temperature.

[1] *Studies on Chemical Dynamics*, translated by Ewen, p. 218.

[2] Le Chatelier, *Compt. rend.*, 1884, **99**, 786.

[3] As the theorem was, at a later date, deduced independently by Braun (*Z. physikal. Chem.*, 1887, **1**, 269), the theorem is also known as the Le Chatelier-Braun theorem or principle.

[4] *Principles of Inorganic Chemistry*, translated by Findlay, 4th edit., p. 59.

[5] The Le Chatelier theorem applies only to changes in stable systems. It does not apply to transformations in metastable systems.

On the other hand, if transference of heat to or from the system is prevented, increase of volume (diminution of pressure) will cause that process to take place which is accompanied by increase of volume, *i.e.* vaporisation. Liquid will therefore pass into vapour, and since this process is accompanied by absorption of heat, the temperature will fall. This is exemplified in the well-known experiment with the cryophorus.

Addition or withdrawal of heat at constant pressure, and increase or diminution of the pressure at constant temperature, will cause the system to pass along lines parallel to the temperature and the pressure axis respectively. The working out of these changes may be left to the reader.

The Clausius-Clapeyron Equation.—While the qualitative changes of equilibrium or the general direction of the equilibrium curve can be predicted by means of the theorem of Le Chatelier, a quantitative formulation of the theorem is given by the thermodynamic equation

$$\frac{dp}{d\mathrm{T}} = \frac{q}{\mathrm{T}(v_2 - v_1)}.$$

In this equation, known as the Clausius-Clapeyron equation, q represents the heat absorbed, per gram, in the transformation of one phase into the other, v_2 and v_1 are the specific volumes of the two phases, and T is the absolute temperature at which the change occurs. The above equation enables one to calculate only the slope of the curve at a given point, not the actual values of the pressure. It is possible, however, to derive an expression by means of which the individual points on the vapour-pressure curve can be calculated approximately.

Referring all quantities to gram-molecular amounts of the substance, and neglecting the volume of the liquid, which is small compared with that of the vapour, we obtain the expression

$$\frac{dp}{d\mathrm{T}} = \frac{\mathrm{Q}}{\mathrm{T} \cdot \mathrm{V}}$$

where Q is the heat absorbed per gram-molecule and V is the volume of a gram-molecule of the vapour. If it be now assumed that the vapour obeys the gas laws, we may write $\mathrm{V} = \frac{\mathrm{RT}}{p}$. Substituting this value in the previous equation, we obtain

$$\frac{1}{p} \cdot \frac{dp}{d\mathrm{T}} = \frac{\mathrm{Q}}{\mathrm{RT}^2}$$

or

$$\frac{d \log_e p}{d\mathrm{T}} = \frac{\mathrm{Q}}{\mathrm{RT}^2}.$$

Finally, if we assume that the heat of reaction (vaporisation) remains constant over the temperature interval $(\mathrm{T}_2 - \mathrm{T}_1)$, the equations just given yield, on integration,

$$\log_{10} p_2 - \log_{10} p_1 = \frac{\mathrm{Q}(\mathrm{T}_2 - \mathrm{T}_1)}{2{\cdot}303 \times 1{\cdot}985 \times \mathrm{T}_1 \times \mathrm{T}_2}.$$

By means of this expression it is possible to calculate, approximately, individual values of the vapour pressure, if one such value is known.

Presence of Complex Molecules.—The Phase Rule, we have seen, takes no account of molecular complexity, and so it is found that the system water—vapour or the system acetic acid—vapour behaves as a univariant system of one component, although in the liquid and sometimes also in the vapour different molecular species (simple and associated molecules) are present. Such systems, however, it should be pointed out, can behave as one-component systems *only if at each temperature there exists an equilibrium between the different molecular species (pseudo-components) in each phase separately and as between the two phases; and only if these equilibria are established sufficiently rapidly*. By this is meant that the time required for establishing equilibrium is short compared with that required for determining the vapour pressure. When these conditions are satisfied, the system will behave as a univariant system of one component.

If, however, a liquid consists of more than one molecular species, and if equilibrium between these species is not continuously and rapidly established, the system liquid—vapour will no longer show the behaviour of a one-component system; the vapour pressure will no longer be a function only of the temperature, but will depend on the relative proportion of the different molecular species in the liquid. In this connection, the investigations of Brereton Baker and his collaborators are of the highest importance.[1]

On subjecting different liquids to intensive drying by means of phosphorus pentoxide, it was found that the boiling-point of the liquid was very greatly raised, as is shown by the numbers in the following table :—

Liquid.	Usual boiling-point.	Boiling-point of intensively dried liquid.
Bromine	63°	118°
Hexane	68·4°	82°
Benzene	80°	106°
Carbon disulphide	49·5°	80°
,, tetrachloride	78°	Above 112°
Ethyl ether	35°	83°
Methyl alcohol	66°	Above 120°
Ethyl alcohol	78·5°	138°

By direct experiment, also, it was found by Baker and Smits [2] that intensively dried benzene could be fractionally distilled, the first fraction boiling at 80° and the residue at 118°. This very dry benzene behaves as a mixture of different molecular species (simple and complex).

It appears, therefore, from these experiments that benzene and the other liquids mentioned behave as unary compounds only because the

[1] *J. Chem. Soc.*, 1912, **101**, 2339; 1922, **121**, 568; 1923, **123**, 1223; 1924, **125**, 1068; 1927, p. 949.

[2] *Ibid.*, 1924, **125**, 1068.

moisture which is present in small amount in the liquids dried in the ordinary way, acts as a catalyst and ensures constant and rapid production of internal equilibrium.

Intensive drying, however, not only fixes the condition of equilibrium, but may also effect a displacement of the internal equilibrium, sometimes in favour of the less and sometimes in favour of the more volatile pseudo-component.[1]

Not only the vapour pressure, but also the vapour density and surface tension of a liquid may be altered by intensive drying. Moreover, in contact with charcoal, ether, methyl alcohol and benzene were found to have a higher vapour pressure than in its absence.

The experimental results referred to above lead to the conclusion that liquids consist of mixtures of different molecular species. In presence of traces of moisture, internal equilibrium between the different molecular species is established rapidly, and the liquid behaves as a unary system, but in absence of moisture, internal equilibrium is not established (or is established very slowly), and the liquid behaves like a multi-component system, the vapour pressure depending not only on the temperature, but also on the amounts of the different molecular species (pseudo-components) in the liquid.

Equilibrium between Solid and Vapour. Sublimation Curve.—Just as in the case of the system liquid—vapour, so also in the case of the system solid—vapour there will be, for each temperature, a certain definite pressure of the vapour; and this pressure will be independent of the relative or absolute amounts of the solid or vapour present, and will depend solely on the temperature.[2] The curve representing the conditions of equilibrium between a solid and its vapour is called a *sublimation curve;* its general form is the same as that of the vaporisation curve.

Although in many cases the sublimation pressure of the solid is immeasurably small, in other cases, *e.g.* camphor,[3] the pressure is considerable. In the table on the following page are given the values of the vapour pressure of ice.[4]

The sublimation curve of all substances, so far as yet found, has its upper limit at the melting-point (triple point), although the possibility of the existence of a superheated solid is not excluded. The lower limit is, theoretically at least, at the absolute zero, provided no new phase, *e.g.* a different crystalline modification, is formed. If the

[1] Smits, *J. Chem. Soc.*, 1926, p. 2655; Smits, de Liefde, Swart and Claassen, *ibid.*, p. 2657.

[2] See footnote 1, p. 7.

[3] Ramsay and Young, *Phil. Trans.*, 1884, **175**, 461; Allen, *J. Chem. Soc.*, 1900, **77**, 413. Even when the vapour pressure of the solid is immeasurably small, the assumption that vapour is given off by a solid substance is justified on theoretical and frequently also on experimental grounds. See Roberts-Austen, *Proc. Roy. Soc.*, 1898, **63**, 454; Spring, *Z. physikal. Chem.*, 1894, **15**, 65; Zenghelis, *ibid.*, 1904, **50**, 219; 1906, **57**, 90.

[4] Scheel and Heuse, *Annalen d. Physik*, 1909 [4], **29**, 723. See aso Thiesen, *ibid.*, p. 1057; Nernst, *Verhand. Deutsch. physikal. Gesell.*, 1909, **11**, 313; 1910, **12**, 565.

VAPOUR PRESSURE OF ICE.

Temperature.	Pressure in mm. mercury.	Temperature.	Pressure in mm. mercury.
− 50°	0·029	− 8°	2·322
− 40°	0·094	− 6°	2·762
− 30°	0·280	− 4°	3·277
− 20°	0·770	− 2°	3·879
− 15°	1·237	0°	4·579
− 10°	1·947		

sublimation pressure of a substance is greater than the atmospheric pressure at any temperature below the point of fusion, then the substance will *sublime without melting* when heated in an open vessel; and fusion will be possible only at a pressure higher than the atmospheric. This is found, for example, in the case of violet phosphorus (p. 62). If, however, the sublimation pressure of a substance at its melting-point is less than one atmosphere, then the substance will melt when heated in an open vessel.

As we have already learned (p. 11), the Phase Rule takes no account of the molecular complexity of the substances participating in an equilibrium. A dissociating substance, therefore, in contact with its vaporous products of dissociation (*e.g.* ammonium chloride in contact with ammonia and hydrogen chloride), will likewise constitute a univariant system of one component, provided the composition of the vapour phase as a whole is the same as that of the solid phase (p. 9). For all such substances, therefore, the conditions of equilibrium will be represented by a curve of the same general form as the vapour-pressure curve of a non-dissociating substance.[1] The same behaviour is also found in the case of substances which polymerise on passing into the solid or liquid state (*e.g.* violet phosphorus). Where such changes in the molecular state occur, however, the time required for equilibrium to be established is, as a rule, greater than when the molecular state is the same in both phases. (See, however, p. 20.)

Changes of sublimation pressure with temperature can be predicted and quantitatively calculated by means of the theorem of Le Chatelier and the Clausius-Clapeyron equation, in the same way as changes of vapour pressure of a liquid (pp. 18 and 19).

Equilibrium between Solid and Liquid. Curve of Fusion.—There is still another univariant system, the existence of which, at definite values of temperature and pressure, the Phase Rule allows us to predict. This is the system solid—liquid. A crystalline solid on being heated to a certain temperature melts and passes into the liquid state; and since this system solid—liquid is univariant, there will be for each temperature a certain definite pressure at which solid and liquid can coexist or be in equilibrium, independently of the amounts

[1] Ramsay and Young, *Phil. Trans.*, 1886, **177**, 87.

of the two phases present. Since the temperature at which the solid phase is in equilibrium with the liquid phase is known as the melting-point or point of fusion of the solid, the curve representing the temperatures and pressures at which the solid and liquid are in equilibrium will represent the change of the melting-point with the pressure. Such a curve is called the *curve of fusion*, or the melting-point curve.

It was not until the middle of the nineteenth century that this connection between the pressure and the melting-point, or the change of the melting-point with the pressure, was observed. The first to recognise the existence of such a relationship was James Thomson,[1] who in 1849 showed that from theoretical considerations such a relationship must exist, and predicted that in the case of ice the melting-point would be lowered by pressure. This prediction was fully confirmed by his brother, W. Thomson [2] (Lord Kelvin). Soon after, Bunsen [3] showed that the melting-point of other substances is also influenced by pressure; and in more recent years ample experimental proof of the change of the melting-point with the pressure has been obtained.

It is easy to predict in a qualitative manner the effect of pressure on the melting-point if we consider the matter in the light of the theorem of Le Chatelier (p. 18). If the pressure on the system solid—liquid be increased, a change will take place which is accompanied by a diminution in volume. If, as in the case of ice and of bismuth,[4] the specific volume of the solid is greater than that of the liquid, increase of pressure will cause the solid to melt. Consequently, the temperature must be lowered in order to counteract the effect of increase of pressure; or, in other words, the melting-point will be lowered by pressure. On the other hand, if, as is usually the case, the passage of the solid to the liquid state is accompanied by an increase of volume, increase of pressure will raise the melting-point.

Quantitatively, the effect of pressure on the melting-point may be calculated by means of the Clausius-Clapeyron equation—

$$\frac{dT}{dp} = \frac{T(v_2 - v_1)}{q}.$$

In the case of the system ice—water, for example, we have the following data: $T = 273°$; specific volume of water $(v_2) = 1{\cdot}0$; specific volume of ice $(v_1) = 1{\cdot}1$; $q = 80$ cals. $= 80 \times 42670$ gram-cm.; $dp =$ 1 atm. $= 1033{\cdot}3$ gm. per sq. cm. Hence,

$$dT = \frac{273 \times (-0{\cdot}1) \times 1033{\cdot}3}{80 \times 42670} = -0{\cdot}00826.$$

Increase of pressure by 1 atm. *lowers* the freezing-point by about 0·0083°. The effect of pressure on the melting-point of ice is therefore

[1] *Trans. Roy. Soc. Edin.*, 1849, **16**, 575.
[2] *Proc. Roy. Soc. Edin.*, 1850, **2**, 267. [3] *Pogg. Annalen*, 1850, **81**, 562.
[4] Tammann, *Z. anorgan. Chem.*, 1904, **40**, 54; Johnston and Adams, *Amer. J. Sci.*, 1911 [4], **31**, 501.

comparatively slight,[1] owing to the small volume-change on fusion and the relatively large value of q. In the case of camphor, the change in the melting-point is much greater, namely, 0·13° per atm. As a general rule, increase of pressure by 1 atm. changes the melting-point by about 0·03°; or, in other words, an increase of pressure of more than 30 atm. is required, on an average, to produce a change in the melting-point of 1°.

The comparatively slight effect produced by pressure on the temperature of equilibrium is characteristic of all systems which are composed only of solid and liquid phases. Such systems are called *condensed systems*.[2]

The values of the fusion pressures of ice, benzene and potassium, given in the following tables (p. 25), will illustrate the course of the fusion curve.[3]

Investigations of the influence of pressure on the melting-point have shown that, up to pressures of several hundred atmospheres, the fusion curve is a straight line.[4] At higher pressures, however, it has been found [5] that the fusion curve no longer remains straight, but bends towards the pressure axis, so that, on sufficiently increasing the pressure, a maximum temperature might at length be reached.[6] This maximum has, so far, however, not been attained, although the melting-point curves of various substances have been studied by Bridgman up to pressures of 12,000 atm. This might be accounted for partly by the fact that the probable maximum temperature in the case of most substances lies at very great pressures, and also by the fact that other solid phases make their appearance, as, for example, in the case of ice (p. 52).

As to the upper limit of the fusion curve, the view has been expressed [7] that, just as in the case of liquid and vapour so also in the

[1] This applies to the effect of "uniform pressure," or pressure acting equally on both phases. When the pressure acts only on one phase the effect is much greater. Thus, when ice only is subjected to pressure, the water being allowed to escape, the melting-point is lowered 0·09° per atmosphere. Non-uniform pressure *always lowers* the melting-point of a crystalline solid (Johnston and Adams, *Amer. J. Sci.*, 1911 [4], **31**, 501).

[2] van't Hoff, *Studies on Chemical Dynamics*, p. 163.

[3] Bridgman, *Z. anorgan. Chem.*, 1912, **77**, 377; *Physical Rev.*, 1914, **3**, 127; 1915, **6**, 1. See also Tammann, *Annalen d. Physik*, 1899 [3], **68**, 564; 1900 [4], **2**, 1, 424; *Z. physikal. Chem.*, 1910, **72**, 609; 1913, **84**, 257.

[4] Barus, *Amer. J. Sci.*, 1892, **42**, 125; Mack, *Compt. rend.*, 1898, **127**, 361; Hulett, *Z. physikal. Chem.*, 1899, **38**, 629. Johnston and Adams (*Amer. J. Sci.*, 1911 [4], **31**, 501) have found that the fusion curve for tin, bismuth, lead, and cadmium, is a straight line up to a pressure of 2000 atm.

[5] Tammann, *Annalen d. Physik*, 1899 [3], **68**, 553, 629; 1900 [4], **1**, 275; **2**, 1; **3**, 161. See also Tammann, *Kristallisieren und Schmelzen* (Leipzig, 1903), or *The States of Aggregation* (London, 1926); Block, *Z. physikal. Chem.*, 1913, **82**, 403; Bridgman, *Physical Rev.*, 1914 [2], **3**, 126, 153; 1915 [2], **6**, 1, 94; Timmermans, *Bull. Acad. roy. Belg.*, 1919, pp. 753, 767.

[6] It has been shown, however, by Bridgman (*Physical Rev.*, 1914 [2], **3**, 126, 153; 1915 [2], **6**, 1, 94) that the curvature of the fusion curve above the pressure of 3000 kgm. per sq. cm. is much less than the curvature below this pressure.

[7] Ostwald, *Lehrbuch*, II., **2**, 373; Poynting, *Phil. Mag.*, 1881 [5], **12**, 2; Planck, *Wied. Annalen*, 1882, **15**, 446; van Laar, *Chem. Weekblad*, 1912, **9**, 744.

FUSION PRESSURE OF ICE.

Temperature.	Pressure in kilogrms. per sq. cm.[1]	Change of melting-point for an increase of pressure of 1 kilogrm. per sq. cm.	Increase of pressure (kilogms. per sq. cm.) required to produce a change of melting-point of 1°.
0°	0	0·0072°	138·5
− 5°	610	0·0087°	115·5
− 10°	1130	0·0102°	98·4
− 15°	1590	0·0118°	84·8
− 20°	1970	0·0135°	74·0

FUSION PRESSURE OF BENZENE.

Pressure in kgm. per sq. cm.	Temperature.	Δv c.c. per gm. $\times 10^6$.	q in gm.-cm. per gm. $\times 10^6$.
1	5·4°	1317	12·88
1,000	32·5°	1026	12·94
2,000	56·5°	872	13·06
3,000	77·7°	759	13·24
4,000	96·6°	675	13·47
5,000	114·6°	614	13·70
6,000	131·2°	564	13·90
7,000	147·2°	522	14·05
8,000	162·2°	485	14·15
9,000	167·7°	451	14·20
10,000	190·5°	422	14·21
11,000	204·2°	394	14·20

FUSION PRESSURE OF POTASSIUM.

Pressure in kgm. per sq. cm.	Temperature.	Δv c.c. per gm. $\times 10^6$.	q in gm.-cm. per gm. $\times 10^6$.
1	62·5°	2680	5·51
1,000	78·7°	2368	5·81
2,000	92·4°	2104	6·02
3,000	104·7°	1877	6·15
4,000	115·8°	1676	6·22
5,000	126·0°	1504	6·21
6,000	135·4°	1347	6·12
7,000	144·1°	1205	6·00
8,000	152·5°	1073	5·85
9,000	160·1°	950	5·67
10,000	167·0°	838	5·43
11,000	173·6°	738	5·16
12,000	179·6°	642	4·83

case of solid and liquid, there exists a critical point at which the solid and the liquid phase become identical. Experimental proof of this view has not, however, so far been obtained.[2]

Although, as we have seen, the vaporisation curve ends at the critical point, the fusion curve may be followed continuously up to temperatures much above the critical temperature for liquid—vapour.[3] Thus the fusion curve of phosphonium chloride (critical point, 49°-50°)

[1] The pressure of 1 atm. is equal to 1·0333 kgm. per sq. cm.: or the pressure of 1 kgm. per sq. cm. is equal to 0·968 atm.

[2] Bakhuis Roozeboom, *Das Heterogene Gleichgewicht*, I., p. 91; Bridgman, *Z. anorgan. Chem.*, 1912, **77**, 377; *Physical. Rev.*, 1914, [2], **3**, 126, 153; 1915 [2], **6**, 1, 94. See, however, Schames, *Verhand. Deutsch. physikal. Gesell.*, 1913, **15**, 1017; *Z. physikal. Chem.*, 1914, **87**, 369.

[3] Tammann, *Arch. Néerland*, 1901 [2], **6**, 244; Bridgman, *Physical Rev*, 1914 [2], **3**, 126, 153.

has been followed up to a temperature of over 100°; and the fusion curve of carbon dioxide (critical point, 31·4°) has been followed up to a temperature of 93·5°. For the course of the fusion curve, therefore, the critical temperature for liquid—vapour appears to have no special significance.

Equilibrium between Solid, Liquid and Vapour. The Triple Point.—From the Phase Rule, $F = n + 2 - r$, it follows that when one component is present in three coexisting phases, the system is invariant. Such a system can exist in stable equilibrium only at one definite temperature and one definite pressure. This definite temperature and pressure at which three phases coexist in equilibrium, as an invariant system, is called a *triple point*. Although the commonest triple point in a one-component system is the triple point, solid, liquid, vapour (S—L—V), other triple points [1] are also possible when, as in the case of ice, sulphur, and other substances, polymorphic forms occur. Whether or not all the triple points can be experimentally realised will, of course, depend on circumstances. We shall, in the first place, consider the triple point S—L—V.

We have already seen that the curve for S—V ends at the melting-point. At this point, liquid and solid are each in equilibrium with vapour at the same pressure, and they must also be in equilibrium with each other; and the particular value of temperature and vapour pressure must lie on the S—V as well as on the L—V curve. At one time it was thought that the S—V curve passes continuously into the L—V curve, but it follows quite clearly from the Clapeyron equation,

$$T\frac{dp}{dT} = \frac{q}{(v_2 - v_1)},$$

that this cannot be so.[2] For the transformation solid → vapour the value of q is greater than for the transformation liquid → vapour, and since $(v_2 - v_1)$ is nearly the same in the two cases, it follows that $\frac{dp}{dT}$ must be greater in the former case than in the latter. That is, the curve for S—V must, in the neighbourhood of the triple point, ascend more rapidly than the curve for L—V. In other words, the two curves must cut each other at the triple point. This is illustrated by the vapour pressure curves for ice and water (Fig. 2).

Since at the triple point S—L—V, solid and liquid must be in equilibrium, it follows that the curve for S—L must also pass through the triple point. We see, therefore, that the triple point is a point of intersection of three univariant curves.

[1] The possible number of triple points in a one-component system is given by the expression $\frac{n(n-1)(n-2)}{1 \cdot 2 \cdot 3}$, where n is the number of phases (Riecke, *Z. physikal. Chem.*, 1890, **6**, 411). The number of triple points, therefore, increases very rapidly, as the number of possible phases increases.

[2] James Thomson, *Phil. Mag.*, 1874 [4], **47**, 447; *Proc. Roy. Soc.*, 1873, **22** 27; Kirchhoff, *Pogg. Annalen*, 1858, **103**, 206.

As to the general arrangement of the three univariant curves around the triple point, the following rules may be given. (1) The prolongation of each of the curves beyond the triple point must lie between the other two curves. (2) The middle position, at one and the same temperature, in the neighbourhood of the triple point is taken by that curve (or its metastable prolongation) which represents the two phases of most widely differing specific volume.[1] That is to say, if a line of constant temperature is drawn immediately above or below the triple point so as to cut the three curves—two stable curves and the metastable prolongation of the third—the position of the curves at that temperature will be such that the middle position is occupied by that curve (or its metastable prolongation) which represents the two phases of most widely differing specific volume.

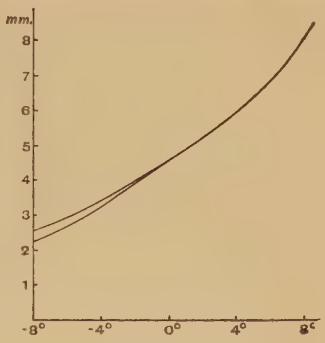

FIG. 2.

Although these rules admit of a considerable variety of possible arrangements of curves around the triple point,[2] only two of these have been experimentally obtained in the case of the triple point solid—liquid—vapour. At present, therefore, we shall consider only these two cases. In Figs. 3 and 4 the curve AO is the sublimation curve, OB the vaporisation curve, and OC the fusion curve.

An examination of these two figures shows that they satisfy the

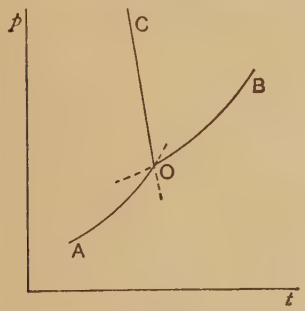

FIG. 3.

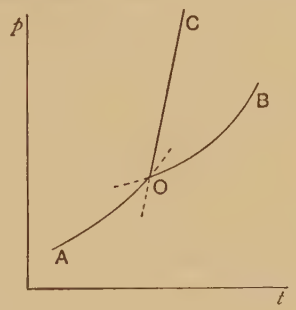

FIG. 4.

rules laid down. Each of the curves on being prolonged passes between the other two curves. In the case of substances of the first type (Fig. 3), the specific volume of the solid is greater than that of the liquid (the substance contracts on fusion); the difference of specific volume will, therefore, be greatest between liquid and vapour. The curve, therefore,

[1] Duhem, *Z. physikal. Chem.*, 1891, **8**, 371.
[2] Roozeboom, *Das Heterogene Gleichgewicht*, I., p. 99.

for liquid and vapour (or its prolongation) must lie between the other two curves; this is seen from the figure to be the case. Similarly, the rule is satisfied by the arrangement of curves in Fig. 4, where the difference of specific volumes is greatest between the solid and vapour. In this case the curve S—V occupies the intermediate position.

As we see, the two figures differ from each other only in that the fusion curve OC in one case slopes to the right away from the pressure axis, thus indicating that the melting-point is raised by increase of pressure; in the other case, the fusion curve slopes to the left, indicating a lowering of the melting-point with the pressure. These conditions are found exemplified in the case of sulphur and ice (pp. 55 and 50). We see further from the two figures, that O in Fig. 3 gives the highest temperature at which the solid can exist, for the curve for solid—liquid slopes back to regions of lower temperature; in Fig. 4, O gives the lowest temperature at which the liquid phase can exist as stable phase.[1]

It should be noted that the triple point S—L—V is not identical with the melting-point as ordinarily determined in an open vessel, that is, under atmospheric pressure. At the triple point, the solid and liquid are in equilibrium under a pressure equal to their vapour pressure. In the case, for example, of ice, the melting-point under atmospheric pressure is at 0° C. At the triple point the pressure is only about 4·6 mm. (p. 22), or nearly 1 atm. less than in the previous case; and since a change in the pressure equal to 1 atm. corresponds with a change in the melting-point of about 0·008° (p. 23), it follows that the melting-point of ice under the pressure of its own vapour will be very nearly + 0·008°. The triple point for ice—water—vapour, therefore, lies at + 0·008°, and at a pressure very slightly in excess of 4·579 mm. (which is the pressure at 0°).

Complexity of the Solid State. Theory of Allotropy.—Attention has already been drawn to the fact that liquids, under ordinary conditions (that is, in presence of traces of moisture), behave as equilibrium mixtures of simple and associated molecules (p. 20). According to the theory of allotropy put forward by Smits,[2] a crystalline solid is a mixed crystal or homogeneous crystalline mixture, built up of molecules of different kinds which undergo transformations leading to an equilibrium. When this inner equilibrium is established continuously and rapidly, a substance behaves as a unary or one-component system; but if the equilibrium is established relatively slowly (as in the case of violet phosphorus), or if the transformations are stopped (*e.g.* by intensive drying), each molecular species acts as a separate component, or pseudo-component. The system, therefore, will not behave as a unary or one-component system, but as a system of a higher order (pseudo-binary, etc.). Dry sulphur trioxide, for

[1] Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 474.

[2] *Z. physikal. Chem.*, 1911, **76**, 421; 1913, **82**, 657; *Die Theorie der Allotropie* (Barth), translation by Smeath Thomas (Longmans).

example, behaves as a mixture; the vapour pressure of the solid can be changed continuously by evaporation, and liquids having different vapour pressures are obtained.[1] According to Smits, therefore, the ordinary melting-point of a unary allotropic substance relates not to a single molecular species, but to an equilibrium mixture of different molecular species (see Chap. X.).

Bivariant Systems.—If we examine Figs. 3 and 4, we see that the curves OA, OB, OC, which represent diagrammatically the conditions under which the systems, solid and vapour, liquid and vapour, solid and liquid, are in equilibrium, form the boundaries of three "fields" or areas. These areas give the conditions of temperature and pressure under which the single phases, solid, liquid and vapour, are capable of stable existence. These different areas are the regions of stability of the phase common to the two curves by which the area is enclosed.[2] Thus, the phase common to the two systems represented by OA (solid and vapour) and OB (liquid and vapour) is the vapour phase; and the area enclosed by the curves AO and OB is therefore the area of the vapour phase. Similarly, the area AOC is the area of the solid phase, and BOC the area of the liquid phase.

Changes at the Triple Point.—If we apply the theorem of Le Chatelier to equilibria at the triple point S—L—V, and ask what changes will occur in such a system when the external conditions of pressure and temperature are altered, the general answer to the question will be: So long as the three phases are present, no change in the temperature or pressure of the system can occur, but *only changes in the relative amounts of the phases;* that is to say, the effect on the system of change in the external conditions is opposed and counterbalanced by the reactions or changes which take place within the system. In discussing these changes, we shall consider first the effect of alteration of the temperature at constant volume and constant pressure, and then the effect of alteration of the pressure both when the temperature remains constant and when it varies.

When the volume is kept constant, the effect of the addition of heat to a system at the triple point S—L—V differs somewhat according as there is an increase or diminution of volume when the solid passes into the liquid state. In the former and most general case (Fig. 4), addition of heat will cause a certain amount of the solid phase to melt, whereby the heat which is added becomes latent; the temperature of the system therefore does not rise. Since, however, the melting of the solid is accompanied by an increase of volume, whereby an increase of pressure would result, a certain portion of the vapour must condense to liquid, in order that the pressure may remain constant. The total effect of addition of heat, therefore, is to cause both solid and vapour to pass into liquid, *i.e.* there occurs the change

[1] Smits and Schoenmaker, *J. Chem. Soc.*, 1924, **125**, 2554, 2573; 1926, pp. 1108, 1603. See also Baker, *ibid.*, 1923, **123**, 1223.

[2] A field is "enclosed" by two curves when these cut at an angle less than two right angles.

$S + V \rightarrow L$. It will, therefore, depend on the relative quantities of solid and vapour, which will disappear first. If the solid disappears first, then we shall pass to the system L—V; if vapour disappears first, we shall obtain the system S—L. Withdrawal of heat causes the reverse change, $L \rightarrow S + V$; at all temperatures below the triple point the liquid is unstable or metastable (p. 38).

When fusion is accompanied by a diminution of volume (*e.g.* ice, Fig. 3), then, since the melting of the solid phase would decrease the total volume, *i.e.* would lower the pressure, a certain quantity of the solid must also pass into vapour in order that the pressure may be maintained constant. On addition of heat, therefore, there occurs the reaction $S \rightarrow L + V$; withdrawal of heat causes the reverse change $L + V \rightarrow S$. Above the temperature of the triple point the solid cannot exist; below the triple point both systems, S—L and S—V, can exist, and it will therefore depend on the relative amounts of liquid and vapour which of these two systems is obtained on withdrawing heat from the system at constant volume.

The same changes in the phases occur when heat is added or withdrawn at constant pressure, so long as the three phases are present. Continued addition of heat, however, at constant pressure will ultimately cause the formation of the bivariant system vapour alone; continued withdrawal of heat will ultimately cause the formation of solid alone. This will be readily understood from Fig. 5. The dotted line D′OD is a line of constant pressure; on adding heat, the system passes along the line OD into the region of vapour; on heat being withdrawn, the system passes along OD′ into the area of solid.

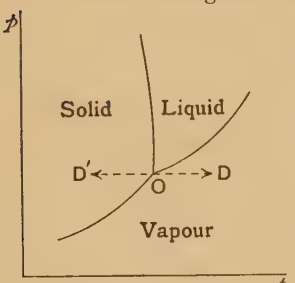

FIG. 5.

Similar changes are produced when the volume of the system is altered. Alteration of volume may take place either while transference of heat to or from the system is cut off (adiabatic change), or while such transference may occur (isothermal change). In the latter case, the temperature of the system will remain constant; in the former case, since at the triple point the pressure must be constant so long as the three phases are present, increase of volume must be compensated by the evaporation of liquid. This, however, would cause the temperature to fall (since communication of heat from the outside is supposed to be cut off), and a portion of the liquid must therefore freeze. In this way the latent heat of evaporation is counterbalanced by the latent heat of fusion. As the result of increase of volume, therefore, the process occurs $L \rightarrow S + V$. Diminution of volume, without transference of heat, will bring about the opposite change, $S + V \rightarrow L$. In the former case there is ultimately obtained the univariant system S—V; in the latter case there will be obtained either S—L or L—V, according as the vapour or solid phase disappears first.

This argument holds good for both types of triple point shown in Figs. 3 and 4 (p. 27). A glance at these figures will show that increase of volume (diminution of pressure) will lead ultimately to the system S—V, for at pressures lower than that of the triple point, the liquid phase cannot exist. Decrease of volume (increase of pressure), on the other hand, will lead either to the system S—L or L—V, because these systems can exist at pressures higher than that of the triple point. If the vapour phase disappears and we pass to the curve S—L, continued diminution of volume will be accompanied by a fall in temperature in the case of systems of the first type (Fig. 3), and by a rise in temperature in the case of systems of the second type (Fig. 4).

Lastly, if the temperature is maintained constant, *i.e.* if heat can pass into or out of the system, then on changing the volume the same changes in the phases will take place as described above until one of the phases has disappeared. Continued increase of volume (decrease of pressure) will then cause the disappearance of a second phase, the

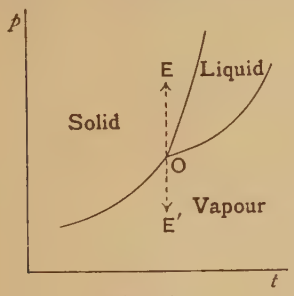

FIG. 6.

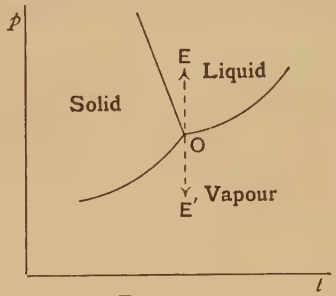

FIG. 7.

system passing along the dotted line OE′ (Figs. 6, 7), so that ultimately there remains only the vapour phase. Conversely, diminution of volume (increase of pressure) will ultimately lead either to solid (Fig. 6) or to liquid alone (Fig. 7), the system passing along the dotted line OE.

In discussing the alterations which may take place at the triple point with change of temperature and pressure, we have considered only the triple point S—L—V. The same reasoning, however, applies *mutatis mutandis*, to all other triple points, so that if the specific volumes of the phases are known, and the sign of the heat effects which accompany the transformation of one phase into the other, it is possible to predict (by means of the theorem of Le Chatelier) the changes which will be produced in the system by alteration of the pressure and temperature.

In all cases of transformation at the triple point, it should be noted that *all three phases are involved in the change*,[1] and not two only ; the fact that in the case, say, of the transformation from solid to liquid, or

[1] Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 474.

liquid to solid, at the melting-point with change of temperature, only these two phases appear to be affected, is due to the presence, as a rule, of a large excess of the vapour phase and to the prior disappearance therefore of the solid or liquid phase.

In the case of triple points at which two solid phases are in equilibrium with liquid, other arrangements of the curves around the triple point are found. It is, however, unnecessary to give a general treatment of these here, since the principles which have been applied to the triple point S—L—V can also be applied to the other triple points.[1]

Polymorphism.—The fact that a solid can exist in more than one crystalline form was first observed by Mitscherlich [2] in the case of sodium phosphate, and later in the case of sulphur. To these two cases others were soon added, at first of inorganic, and later of organic substances, so that polymorphism is now recognised as of very frequent occurrence indeed. These various forms of a substance differ in the form of the crystal lattice or in the distance apart of the lattice points, and this difference manifests itself not only in crystalline shape, but also in melting-point, specific gravity, and other physical properties. In the liquid state, however, the differences do not exist.[3]

According to the definition of phases (p. 6), each of these polymorphic forms constitutes a separate phase of the particular substance. As is readily apparent, the number of possible systems formed of one component may be considerably increased when that component is capable of existing in different crystalline forms. We have, therefore, to inquire what are the conditions under which different polymorphic forms can coexist, either alone or in presence of the liquid and vapour phase.

From the equation $F = n + 2 - r$, it is clear that zero variability is obtained when one component exists in three phases. From this it follows that one component cannot exist as a stable system in more than three phases, for in that case the system would have a negative variability, and this is impossible. Two different crystalline forms of a substance, therefore, can coexist in stable equilibrium only with vapour or with liquid, not with both vapour and liquid. Two new triple points, therefore, become possible, namely, S_1—S_2—V and S_1—S_2—L, where S_1 and S_2 denote the two different crystalline forms.

Triple Point S_1—S_2—V. Transition Point. — Just as the triple point S—L—V is the point of intersection of the two univariant curves S—V and L—V, so the triple point S_1—S_2—V is the point of intersection of the two curves S_1—V and S_2—V. Below the triple point only one of the solid phases (S_1) can exist in stable equilibrium with vapour; above the triple point only the other solid phase (S_2) will be stable. The triple point S_1—S_2—V is, therefore, a point at which the relative stability of the two solid phases undergoes change.

[1] Roozeboom, *Das Heterogene Gleichgewicht*, I., p. 189.
[2] *Annales chim. et phys.*, 1821, **19**, 414.
[3] See, however, Smits' theory of allotropy, p. 28.

The triple point S_1—S_2—V is the point of intersection not only of the curves for the two univariant systems S_1—V and S_2—V, but the point of intersection also of a third curve, that for the system S_1—S_2. Since this is also a univariant system, the temperature at which the two solid phases can coexist will depend on the pressure. When the pressure is the atmospheric pressure, the temperature at which the two solid phases can coexist, and at which the relative stability of the two forms undergoes change, is known as the *transition point.* The transition point, therefore, bears the same relation to the triple point S_1—S_2—V as the melting-point does to the triple point S—L—V.

In the table below is given a list of some of the more important polymorphic substances, and the temperatures of the transition point.[1]

Substance.	Transition temperature.
Ammonium nitrate—	
α-rhombic → β-rhombic	32·3°
β-rhombic → rhombohedral	84·2°
Rhombohedral → cubic	125·2°
Mercuric iodide	126°
Potassium nitrate	129°
Silver iodide	145°
„ nitrate	159·6°
Sulphur	95·5°
Tetrabrommethane	46·8°
Thallium nitrate—	
Rhombic → rhombohedral	80°
Rhombohedral → regular	142·5°
Thallium picrate	44°
Tin	18°

By some investigators the transition temperature has been found to vary somewhat according to the previous history of the substance, a behaviour interpreted by Smits as confirming his view (p. 28) that polymorphic forms are equilibrium mixtures of different molecular species. The necessity of making sure that one is dealing with a pure homogeneous solid and not with a mixture of polymorphous forms must also be emphasised (p. 46).

In the preceding discussion the transition point S_1—S_2—V has been regarded as the point of intersection of the vapour-pressure curves of the two solid forms, and equality of the vapour pressure has been taken as the condition for the stable coexistence of two crystalline forms of a substance. Were one dependent, however, on measurements of vapour pressure and temperature, the determination of the transition point would be a matter of great and in some cases of insuperable

[1] Zawidski, *Z. physikal. Chem.*, 1904, **47**, 727; van Eyk, *ibid.*, 1905, **51**, 720; Jänecke, *ibid.*, 1915, **90**, 280, 313; Cohen and Moesveld, *ibid.*, 1913, **85**, 419; 1920, **94**, 450; Cohen and Helderman, *ibid.*, 1914, **87**, 409; 1915, **89**, 493, 638, 728, 733, 742; Cohen and van den Bosch, *ibid.*, 1915, **89**, 757; Early and Lowry, *J. Chem. Soc.*, 1919, **115**, 1387; Cohen and Kooy, *Z. physikal. Chem.*, 1924, **109**, 81; Bridgman, *J. Amer. Chem. Soc.*, 1914, **36**, 1344. For a study of mercuric iodide, see Smits and Bokhorst, *Z. physikal. Chem.*, 1914-15, **89**, 365, 374; Smits, *ibid.*, 1916-18, **92**, 345; Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581; Losana, *Gazzetta*, 1926, **56**, 301.

difficulty. When it is considered, however, that not only the vapour pressure but also the other physical properties of the solid phases, *e.g.* the density, undergo an abrupt change on passing through the transition point, owing to the transformation of one form into the other, then any method by which this abrupt change in the physical properties can be detected may be employed for determining the transition point. A considerable number of such methods have been devised, and a description of the most important of these is given in the Appendix.

Transition Curve.—The transition point, like the melting-point, is influenced by pressure, and in this case also it is found that pressure may either raise or lower the transition point. The transition curve, therefore, may be inclined either away from or towards the pressure axis. The direction of the transition curve can be predicted, on the basis of the theorem of Le Chatelier, if the change of volume accompanying the passage of one form into the other is known. The quantitative influence of pressure on the transition point can be calculated by means of the Clapeyron equation $\frac{dT}{dp} = \frac{T(v_2 - v_1)}{q}$. Since, as in the case of all condensed systems the value of $(v_2 - v_1)$ is small, the transition point, like the melting-point, is altered only to a relatively small extent by pressure.

The transformation, for example, of the α-rhombic to the β-rhombic form of ammonium nitrate is accompanied by an increase of volume ($v_\beta - v_\alpha = 0{\cdot}0220$ c.c. per gram).[1] $\frac{dT}{dp}$ has, therefore, a positive value, or the transition point is raised by increase of pressure, as shown by the numbers in the following table :—[2]

Pressure in kgm. per sq. cm.	Temperature.
1	32·0°
200	38·5°
400	45·4°
600	52·9°
800	60·8°

On the other hand, the passage of the β-rhombic into the rhombohedral form of ammonium nitrate is accompanied by a contraction, and the transition point is therefore lowered by increase of pressure, as shown by the following numbers :—[3]

Pressure.	Temperature.
1 atm.	85·85°
100 ,,	84·38°
200 ,,	83·03°
250 ,,	82·29°

[1] Cohen and Kooy, *Z. physikal. Chem.*, 1924, **109**, 81. The heat of transformation is 4·99 cal. per gram (Cohen and Helderman, *Z. physikal. Chem.*, 1924, **113**, 145).

[2] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581.

[3] Lussana, *Nuovo Cim.*, 1895 [4], **1**, 105.

The fairly numerous investigations which have been carried out show that over a range of pressure of a few hundred atmospheres the transition curve is practically a straight line. If, however, the range of pressure is extended considerably, up to say 12,000 atm., the transition curve ceases to be linear and shows a more or less marked curvature, being sometimes convex and sometimes concave to the pressure axis.[1]

In the case of mercuric iodide, as also in the case of Glauber's salt (a two-component system), it has been found that with increase of pressure the transition curve passes through a point of maximum temperature, and exhibits, therefore, a form similar to that assumed by Tammann for the fusion curve.[2]

In the following table are given the values of pressure and temperature for the transition point of red and yellow mercuric iodide:—[3]

Pressure in kgm. per sq. cm.	Temperature.	Δv c.c. per gm. $\times 10^5$.	q in gm.-cm. per gram $\times 10^5$.	$\frac{dT}{dp}$.
1	127·0°	342	0·513	0·0267
1,000	149·8°	217	0·491	0·0187
2,000	165·2°	127	0·456	0·0122
3,000	174·9°	65	0·420	0·0069
4,000	179·9°	24	0·390	0·0028
5,000	181·2°	— 8	0·365	— 0·0010
6,000	178·2°	— 45	0·345	— 0·0059
7,000	169·7°	— 100	0·330	— 0·0134
8,000	152·4°	— 175	0·318	— 0·0234
9,000	122·3°	— 270	0·296	— 0·0361
10,000	79·4°	— 390	0·278	— 0·0495

Enantiotropy and Monotropy.—The triple point S_1—S_2—V is one at which reversible transformation of the two crystalline forms can take place. Two cases must now be distinguished: (1) The transition point under atmospheric pressure lies below the melting-point of the solid; (2) the transition point lies above the melting-point. In the former case, each form possesses a definite range of stable existence, and is capable of undergoing reversible transformation into the other. In the latter case, only one of the solid forms is stable at all temperatures up to the melting-point, the other solid form being metastable. In this case there is no transition point realisable at atmospheric pressure, and transformation of crystalline forms can take place *only in one direction.* These two different kinds of behaviour are distinguished by the names *enantiotropy* and *monotropy;* enantiotropic substances being such that the change of one form into the other is a

[1] Bridgman, *Proc. Nat. Acad. Sci.*, 1915, **1**, 513; *Proc. Amer. Acad. Arts Sci.*, 1916, **51**, 581; Tammann, *Nachr. Ges. Wiss. Göttingen*, 1915, 59.
[2] *Z. physikal. Chem.*, 1903, **46**, 818.
[3] Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1915, **51**, 55.

reversible process (*e.g.* rhombic sulphur into monoclinic, and monoclinic sulphur into rhombic), and monotropic substances, those in which the transformation of the crystalline forms is irreversible. This is found, for example, in the case of iodine monochloride and benzophenone.[1]

These differences of behaviour can be explained very well in many cases by supposing that in the case of enantiotropic substances the transition point lies below the melting-point, while in the case of monotropic substances, it lies above the melting-point.[2] These conditions would be represented by the Figs. 8 and 9.

In these two figures, O_3 is the transition point, O_1 and O_2 the melting-points of the metastable and stable forms respectively. From Fig. 9 we see that the crystalline form I., at all temperatures up to its melting-point, is metastable with respect to the form II. In such cases the transition point could be reached only at higher pressures.

Although, as already stated, this explanation suffices for many cases, it does not prove that in all cases of monotropy the transition

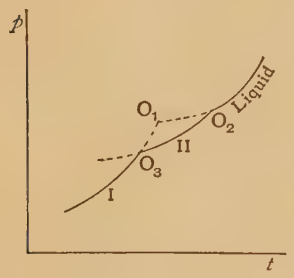

FIG. 8.

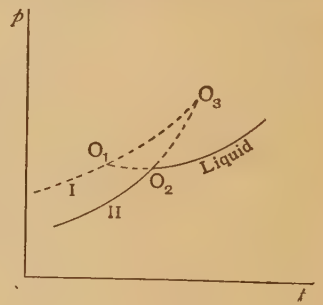

FIG. 9.

point is above the melting-point of the two forms. It is also quite possible that the transition point may lie below the melting-points;[3] in this case we have what is known as *pseudomonotropy*. It is possible that graphite and diamond,[4] perhaps also the two forms of phosphorus, stand in the relation of pseudomonotropy (*v.* p. 64). The possibility must also be recognised that there may be no transition point, real or imaginary, at all, but that the two crystalline forms may behave as

[1] The two forms of iodine monochloride melt at 13·9° and 27·2°, while those of benzophenone melt at 26° and 48°. In the case of menthol four crystalline forms have been obtained melting at 31·5°, 33·5°, 35·5°, and 42·5°. Only the last form is stable (Wright, *J. Amer. Chem. Soc.*, 1917, **39**, 1515).

[2] Lehmann, *Molekularphysik*, I., 193 (1888); Schaum, *Annalen*, 1897, **300**, 215; Ostwald, *Z. physikal. Chem.*, 1897, **22**, 313.

[3] Roozeboom, *Das Heterogene Gleichgewicht*, I., p. 177.

[4] *Ibid.*, p. 179. For discussions of the diamond problem and of the diagram of states of carbon, see Baur, Sichling, and Schenker, *Z. anorgan. Chem.*, 1915, **92**, 313; Lewis and Randall, *J. Amer. Chem. Soc.*, 1915, **37**, 462; Parsons, *Phil. Trans.*, 1919, A. **220**, 67; van Liempt, *Z. anorgan. Chem.*, 1921, **115**, 218; Tammann, *ibid.*, 1921, **115**, 145.

dynamic isomerides. The system will then become a binary one (see Chap. X.).

The disposition of the curves in Figs. 8 and 9 also explains the phenomenon sometimes met with, especially in organic chemistry, that the substance first melts, then solidifies, and re-melts at a higher temperature. On again determining the melting-point after re-solidification, only the higher melting-point is obtained.

The explanation of such a behaviour is, that if the determination of the melting-point is carried out rapidly, the point O_1, the melting-point of the metastable solid form, may be realised. At this temperature, however, the liquid is metastable with respect to the stable solid form, and if the temperature is not allowed to rise above the melting-point of the latter, the liquid may solidify. The stable solid modification thus obtained will melt only at a higher temperature.

Another representation of enantiotropy and monotropy has been put forward by A. Smits,[1] on the basis of his theory of allotropy. According to this theory, polymorphism and allotropy in general are explained as being due to the existence of two or more molecular species which coexist in equilibrium in each phase. Difference in crystalline form can then be explained as due to difference in the equilibrium proportions of the molecular species. Each phase, therefore, is a mixture of different kinds of molecules which undergo transformations leading to a chemical equilibrium. According to this theory, the equilibrium diagram for polymorphic substances becomes more complicated than is indicated in the present chapter, since the systems cease to be strictly unary and become binary (pseudo-binary) or even of a higher order. The theory has much to commend it, and although it still lacks complete experimental confirmation,[2] it offers some help towards a more adequate interpretation of the equilibrium relations of polymorphic substances.[3]

The subject will be discussed more fully at a later point (Chap. X.).

Enantiotropy combined with Monotropy.—Not only can polymorphic substances exhibit enantiotropy or monotropy, but, if the substance is capable of existing in more than two crystalline forms, both relationships may be found, so that some of the forms may be enantiotropic to one another, while the other forms exhibit only monotropy. This behaviour is seen, for example, in the case of sulphur, which can exist in as many as eight different crystalline varieties. Of these only monoclinic and rhombic sulphur exhibit the relationship of enantiotropy, *i.e.* they possess a definite transition point, while the other forms are all metastable with respect to rhombic and monoclinic

[1] *Z. physikal. Chem.*, 1911, **76**, 421; 1913, **82**, 657; *Die Theorie der Allotropie* (Barth, 1921), translation by Smeath Thomas (Longmans); Terwen, *Z. physikal. Chem.*, 1916, **91**, 443.

[2] See criticism, for example, by Tammann, *Z. physikal. Chem.*, 1913, **83**, 728; **84**, 753.

[3] See Jänecke, *Z. physikal. Chem.*, 1915, **90**, 280, 313; Cohen, *Trans. Faraday Soc.*, 1915, **10**, 216.

sulphur, and remain so up to the melting-point; that is to say, they are monotropic modifications.[1]

Suspended Transformation. Metastable Equilibria.—In the preceding pages we have considered only systems in stable equilibrium, and we have assumed that when the external conditions rendered a change of phase possible, that change took place. In actual fact, however, this is by no means always the case. Transformation may remain suspended.

It has, for example, long been known that water can be cooled below zero without solidification occurring. This was first discovered in 1724 by Fahrenheit,[2] who found that water could be exposed to a temperature of $-9{\cdot}4^\circ$ without solidifying; so soon, however, as a small particle of ice was brought in contact with the water, crystallisation commenced. Superfused or supercooled water—*i.e.* water cooled below 0°—is unstable only in respect of the solid phase; so long as the presence of the solid phase is carefully avoided, the water can be kept for any length of time without solidifying, and the system, supercooled water and vapour, behaves in every way like a stable system. A system which in itself is stable, and which becomes instable only in contact with a particular phase, is said to be *metastable*, and the region throughout which this condition exists is called the metastable region.[3] Supercooled water, therefore, is in a metastable condition. If the supercooling be carried below a certain temperature, solidification takes place spontaneously without the addition of the solid phase; the system then ceases to be metastable, and becomes *instable*.

Suspended transformation is likewise found to occur at the transition point for two crystalline forms of a substance. The transition point, as we have seen, is analogous to the melting-point of a solid. In both cases the change of phase is associated with a definite temperature and pressure in such a way that below the point the one phase, above the point the other phase, is stable. The transition point, however, differs in this respect from a point of fusion that while it is possible to supercool a liquid, no definite case is known where the solid has been heated above its melting-point without passing into the liquid state. Transformation, therefore, is suspended only on one side of the melting-point. In the case of two solid phases, however, the transition point can be overstepped in both directions, so that each phase can be obtained in the metastable condition. Thus, rhombic sulphur can be heated above the transition point, and monoclinic sulphur can be obtained at temperatures below the transition point, although in both cases transformation into a more stable form is possible; the system becomes metastable.[4]

[1] Brauns, *Jahrb. Min. Beil.-Bd.*, 1900, **13**, 39. [2] *Phil. Trans.*, 1724, **39**, 78.

[3] The permanence or apparent permanence of a metastable system may be due to the fact that no nuclei of the stable phase are formed or that their number is negligible, or to the fact that the velocity of transformation is very slow. Only in the former case is the system truly metastable (see also pp. 41 ff.). Cf. Othmer, *Z. anorgan. Chem.*, 1915, **91**, 219.

[4] See Cohen and Moesveld, *Z. physikal. Chem.*, 1920, **94**, 450, 471; Cohen and Bruins, *ibid.*, 1920, **94**, 465.

The same reluctance to form a new phase is observed also in the phenomena of superheating of liquids, and the "hanging" of mercury in barometers, in which case the vapour phase is not formed. In general, then, we may say that *a new phase will not necessarily be formed immediately the system passes into such a condition that the existence of that phase is possible;* but rather, instead of the system undergoing transformation so as to pass into the most stable condition under the existing pressure and temperature, this transformation will be "suspended" or delayed, and the system will become metastable. Only in the case of the formation of the liquid from the solid phase, in a one-component system, has this reluctance to form a new phase not been observed.[1]

To ensure the formation of a new phase and to prevent the occurrence of suspended transformation, it is necessary to have that phase present. The presence of the solid phase will prevent the supercooling of a liquid (hence the efficacy of "inoculation" or "seeding"); and the presence of the vapour phase will prevent the superheating of a liquid. Suspended transformation takes place more readily in the case of the passage of an isotropic into an anisotropic phase (*e.g.* liquid into crystalline solid), where a definite arrangement of the molecules in a space lattice is necessary, than in the case of the transformation of one isotropic phase into another isotropic phase, where the molecules are in disarray.

As to the amount of the new phase required to bring about the transformation of the metastable phase, quantitative measurements have been carried out only in the case of the initiation of crystallisation in a supercooled liquid.[2] As the result of these investigations, it was found that, in the case of superfused salol, the very small amount of 1×10^{-7} gm. of the solid phase is sufficient to induce crystallisation. Crystallisation of a supercooled liquid, however, can be initiated only by a "nucleus" of the same substance in the solid state, or, as has also been found, by a nucleus of an isomorphous solid phase; it is not brought about by the presence of any chance solid. It would also appear that crystallisation of a supercooled liquid may also be initiated, without the presence of the solid phase, by shock or other mechanical stimulus.[3]

When transformation of a less stable into a more stable phase occurs, the change does not take place at one moment throughout the whole phase, but proceeds from definite points or growth centres (nuclei). Such "nuclei" may form spontaneously in a supercooled phase, as is seen, for example, in the cloud formation produced on the cooling of a vapour by adiabatic expansion. The influence of dust particles and of gaseous ions in increasing the number of condensation nuclei, is well known.

[1] In this connection, see Pawloff, *Z. physikal. Chem.*, 1908, **65**, 1, 545; Tammann, *ibid.*, 1909, **68**, 257; Berthoud, *J. Chim. phys.*, 1910, **8**, 337.

[2] Ostwald, *Z. physikal. Chem.*, 1897, **22**, 289.

[3] Young and Sickels, *J. Amer. Chem. Soc.*, 1913, **35**, 1067.

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In the case of a supercooled liquid, spontaneous formation of nuclei or crystal growth centres also takes place. Since, however, an anisotropic phase, with definite molecular arrangement, must now be formed from an isotropic phase, the number of nuclei formed in a given time per unit mass of the substance will be less than in the case of transformations between isotropic phases.

On investigating the spontaneous formation of growth centres in supercooled liquids, Tammann [1] found that the number of nuclei per unit mass of substance formed in a given time depends on the degree of supercooling, and attains a maximum value at a certain degree of supercooling which varies from substance to substance. Thus, in the case of piperine (m.p. 129°), Tammann found that the maximum formation of nuclei takes place at 40°, and that the tendency to spontaneous crystallisation becomes negligible at 80° and at 0°. Impurities may increase or decrease very greatly the number of nuclei formed without, however, greatly affecting the temperature of maximum formation.[2] The temperature of maximum formation of nuclei is raised by increase of pressure.[3] In the case of piperine the temperature of maximum formation was raised from 35° to 70° by an increase of pressure of 1000 kgm. per sq. cm. It has also been found by Othmer [4] that the number of crystal growth centres formed at a given temperature in a supercooled liquid is all the smaller the higher the temperature to which the liquid is heated before cooling.

Pressure-Temperature Relations between Stable and Metastable Forms.—Since the possibility of the existence of a substance in a metastable state must be recognised, it becomes of importance to consider what relationship exists between the vapour pressure of the stable and metastable forms.

It has already (p. 26) been pointed out that in the neighbourhood of the triple point S—L—V, the curve for S—V must ascend more rapidly than the curve for L—V. It follows, therefore, that if the curve for L—V be continued downwards to temperatures below the triple point, the continuation of the curve must lie above the curve for S—V. In other words, the vapour pressure of a supercooled liquid (metastable system) must be higher than the vapour pressure of the solid (stable system) at the same temperature. This conclusion is indicated by the curves for ice and water in Fig. 2 (p. 27), and is borne out by the numbers in the table on the following page.

It is now easy to understand why ice, water, and vapour cannot coexist in equilibrium at temperatures below the triple point. Since the vapour pressure of the supercooled water is greater than that of ice, vapour will condense on the ice, and a process of distillation will

[1] *Z. physikal. Chem.*, 1898, **25**, 472.

[2] For influences affecting the spontaneous crystallisation of super-cooled liquids, see also Hinshelwood and H. Hartley, *Phil. Mag.*, 1922 [6], **43**, 78; Schaum, *Z. anorgan. Chem.*, 1921, **120**, 241.

[3] Hasselblatt, *Z. anorgan. Chem.*, 1921, **119**, 353.

[4] *Z. anorgan. Chem.*, 1915, **91**, 235.

VAPOUR PRESSURE OF ICE AND OF SUPERCOOLED WATER.

Temperature.	Pressure in mm. mercury.		
	Water.	Ice.	Difference.
0°	4·579	4·579	0·000
− 2°	3·952	3·879	0·073
− 4°	3·404	3·277	0·127
− 8°	2·509	2·322	0·187
− 10°	2·144	1·947	0·197

take place from the water to the ice till all the water will have disappeared and only ice and vapour remain.[1]

Since in the neighbourhood of the triple point S_1—S_2—V the curves S_1—V and S_2—V are arranged similarly to the curves S—V and L—V in the neighbourhood of the triple point S—L—V, it follows that in the case of two crystalline forms of a substance, the metastable form will, at a given temperature, have a higher vapour pressure than the stable form. The vapour pressure curve, for example, of rhombic sulphur must at temperatures above 95·5° (the transition point) lie above that for the stable form, monoclinic sulphur; and at temperatures below the transition point the vapour pressure curve for monoclinic sulphur must lie above that for rhombic sulphur (p. 54).

Quite generally, then, we can say that *in a one-component system the vapour pressure of a metastable phase is, at a given temperature, greater than that of the stable phase.*

Velocity of Transformation of Metastable Systems.—Although the presence of the more stable form of a substance may ensure that transformation of the metastable system takes place, the rate at which this transformation occurs may vary very greatly. In some cases, the change may take place so quickly as to appear almost instantaneous, while in other cases the change takes place so slowly as to require hundreds of years for its achievement.

In this connection, most attention has been paid to the study of the velocity of crystallisation of a supercooled liquid, the first experiments in this direction having been made by Gernez[2] on the velocity of crystallisation of phosphorus and sulphur. Since that time, the velocity of crystallisation of other supercooled liquids has been investigated; such as acetic acid and phenol by B. Moore;[3] supercooled water by Tumlirz and by Walton and Judd;[4] and a number of organic

[1] This phenomenon of distillation from the super-cooled liquid to the solid has been very clearly observed in the case of furfuraldoxime (V. Goldschmidt, *Z. Kryst.*, 1897, **28**, 169).

[2] *Compt. rend.*, 1882, **95**, 1278; 1884, **97**, 1298, 1366, 1433.

[3] *Z. physikal. Chem.*, 1893, **12**, 545.

[4] *Sitzungsber. Wiener. Akad.*, 1894, **103**, IIa, 226; *J. Physical Chem.*, 1914, **18**, 722. See also Hartmann, *Z. anorgan. Chem.*, 1914, **88**, 128.

substances by Tammann,[1] Friedländer and Tammann,[2] and by Bogojawlenski.[3]

In measuring the velocity of crystallisation, the supercooled liquids were contained in narrow glass tubes, and, after crystallisation had been started by " inoculation," the time required for the crystallisation to advance along a certain length of the tube was determined, the velocity being expressed in millimetres per minute. The internal diameter of the tube and the thickness of the walls are, however, important factors in affecting the rate of growth of crystals in a supercooled liquid.[4] The results which have so far been obtained may be summarised as follows. For any given degree of supercooling of a substance, the velocity of crystallisation is constant. As the degree of supercooling increases, the velocity of crystallisation also increases, until at a certain temperature (about 20°-30° below the melting-point) the velocity of crystallisation attains a maximum value which is definite and characteristic for each substance.[5] This maximum velocity remains constant over a certain range of temperature ;[6] thereafter, the velocity diminishes fairly rapidly, and, with sufficient supercooling, may become zero.

Since the temperature at which the spontaneous formation of crystal nuclei has its maximum value is, in general, below that at which the velocity of crystallisation is a maximum, it is possible, by rapid cooling, to pass through the temperatures of maximum crystallisation velocity and maximum formation of nuclei, and to obtain the liquid at a temperature at which the velocity of crystallisation (and also of crystal nuclei formation) becomes negligible. Since the viscosity increases with fall of temperature, the liquid passes into a glassy mass, which will remain (practically) permanent even in contact with the crystalline solid.[7] Some substances can be supercooled to the glassy state more readily than others.

In ordinary glass we have a familiar example of a liquid which has been cooled to a temperature at which crystallisation takes place with very great slowness. If, however, glass is heated, spontaneous formation of nuclei takes place and a temperature is reached, much below the melting-point of the glass, at which crystallisation occurs with

[1] *Z. physikal. Chem.*, **23-29.** See also Küster, *ibid.*, **25-28**; Müller, *ibid.*, 1914, **86,** 177.

[2] *Z. physikal. Chem.*, 1897, **24,** 152.

[3] *Ibid.*, 1898, **27,** 585.

[4] Walton and Judd, *J. Physical Chem.*, 1914, **18,** 722.

[5] Pressure appears to decrease the maximum crystallisation velocity (Hasselblatt, *Z. anorgan. Chem.*, 1921, **119,** 325).

[6] In the case of certain substances the velocity of crystallisation does not remain constant within this range of temperature, but may increase or decrease. This behaviour is attributed to differences in the molecular complexity of the liquid and solid substances (Tammann, *Gedenkboek aangeboden aan J. M. van Bemmelen*, 1910, p. 297.

[7] See Tammann (*Z. physikal. Chem.*, 1898, **25,** 472) for an investigation of the conversion of liquids into glasses by cooling.

appreciable velocity. We then observe the phenomenon of devitrification.[1]

When the velocity of crystallisation is studied at temperatures above the maximum point, it is found that the velocity is diminished by the addition of foreign substances; and in some cases it has been found that the diminution is proportional to the square root of the concentration of the dissolved substance, and is the same for equimolecular quantities of different substances. It would hence appear possible to utilise this behaviour as a method for determining molecular weights.[2] The rule is, however, by no means a universal one. Thus it has been found by F. Dreyer,[3] in studying the velocity of crystallisation of formanilide, that the diminution in the velocity produced by equivalent amounts of different substances is not the same, but that the foreign substances exercise a specific influence. Similar results, out of harmony with von Pickardt's rule, have been obtained by other investigators,[4] and the specific nature of the influence of foreign substances on the velocity of crystallisation of a supercooled liquid must be recognised.

In their investigation of the influence of foreign substances on the velocity of crystallisation of supercooled water, Walton and Brann [5] found that when the added substance contained less than eight atoms, the retardation of the velocity of crystallisation is specific, and that when the number of atoms is greater than eight, the velocity of crystallisation is all the lower the greater the number of atoms in the added substance.

Marc [6] and Freundlich [7] have put forward the view that the velocity of crystallisation of supercooled liquids is influenced by adsorption phenomena, the dissolved substance being adsorbed on the surface of the crystals. In this connection, Freundlich and Oppenheimer [8] have shown that the crystallisation velocity of supercooled water is frequently, if not always, increased by colloidal substances the particles of which are non-spherical, whereas particles which are spherical, and also the truly dissolved substances, lower the velocity.

It may further be stated that von Pickardt's rule does not hold when the foreign substance forms mixed crystals (Chap. VIII.) with the crystallising substance.[9]

[1] W. Guertler, *Z. anorgan. Chem.*, 1904, **40**, 268; Tammann, *Z. Elektrochem.*, 1904, **10**, 532; *Z. anorgan. Chem.*, 1914, **87**, 248.

[2] E. von Pickardt, *Z. physikal. Chem.*, 1902, **42**, 17.

[3] *Z. physikal. Chem.*, 1904, **48**, 467.

[4] Padoa and Galeati, *Gazzetta*, 1904, **35**, I. 181; Walton and Brann, *J. Amer. Chem. Soc.*, 1916, **38**, 317, 1161; Brann, *ibid.*, 1918, **40**, 1168.

[5] *J. Amer. Chem. Soc.*, 1916, **38**, 317, 1161; Brann, *ibid.*, 1918, **40**, 1168.

[6] *Z. physikal. Chem.*, 1908, **61**, 385; 1909, **67**, 470; **68**, 104; 1910, **73**, 685; **75**, 710.

[7] *Ibid.*, 1910, **75**, 245.

[8] *Ber.*, 1925, **58**, 143.

[9] Padoa, *Accad. Lincei, Atti*, 1904, **13**, 329; Freundlich, *Z. physikal. Chem.*, 1911, **75**, 245. For a study of the crystallisation velocity of isomorphous mixtures, see Hasselblatt, *Z. physikal. Chem.*, 1913, **83**, 1.

Whereas the transformation of a metastable, supercooled liquid into the stable solid phase takes place fairly rapidly, if the degree of supercooling has not been too great, the corresponding transformation of metastable polymorphic forms may take place only with great slowness. Thus, although calcite is the most stable form of calcium carbonate at the ordinary temperature,[1] the metastable modification, aragonite, nevertheless exists under the ordinary conditions in an apparently very stable state.

In the case of sulphur, also, transformation of the metastable monoclinic sulphur into the stable rhombic form may take place at the ordinary or at lower temperatures with very great slowness. Sainte Claire Deville, for example, has stated [2] that a specimen of monoclinic sulphur, kept at the ordinary temperature, had not undergone complete transformation into the more stable rhombic form even after a period of eight years.

Ordinary white tin, also, although apparently possessing permanence, is in reality in a metastable state, under the ordinary conditions of temperature and pressure; and this great degree of permanence, and the apparent stability which makes possible the everyday use of this metal, are due to the sluggishness with which transformation into the stable grey form occurs (p. 58).

The behaviour found in the case of sulphur and of tin is met with also in the case of all transformations in the solid state, but the velocity of the change is less in some cases than in others, and appears to decrease with increase of the valency of the element.[3] To this fact van't Hoff attributes the great permanence of many really unstable (or metastable) carbon compounds.

The velocity of transformation can be accelerated by various means. One of the most important of these is the employment of a liquid which has a solvent action on the solid phases. Just as we have seen that at any given temperature the less stable form has the higher vapour pressure, but that at the transition point the vapour pressure of both forms becomes identical, so also it can be proved theoretically, and be shown experimentally, that at a given temperature the solubility of the less stable form is greater than that of the more stable, but that at the transition point the solubility of the two forms becomes identical.[4] If, then, the two solid phases are brought into contact with a solvent, the less stable phase will dissolve more abundantly than the more stable; the solution will therefore become supersaturated with respect to the latter, which will be deposited. A

[1] Foote, *Z. physikal. Chem.*, 1900, **33**, 740. See also Sosman, Hostetter, and Merwin, *J. Washington Acad. Sci.*, 1915, **5**, 563; Johnston, Merwin, and Williamson, *Amer. J. Sci.*, 1916, **41**, 473.

[2] *Compt. rend.*, 1847, **25**, 857. Cohen, *Z. physikal. Chem.*, 1924, **109**, 109.

[3] Van't Hoff, *Arch. Néerland.*, 1901, **6**, 471.

[4] See, for example, the determinations of the solubility of rhombic and monoclinic sulphur, by J. N. Brönsted, *Z. physikal. Chem.*, 1906, **55**, 378; also solubilities of polymorphic phthalylhydrazides (Chattaway and Lambert, *J. Chem. Soc.*, 1915, **107**, 1773).

gradual change of the less stable form, therefore, takes place, through the medium of the solvent. In this way the more rapid conversion of white tin into grey in presence of a solution of tin ammonium chloride (p. 58) is to be explained. Although, as a rule, solvents accelerate the transformation of one solid phase into the other, they may also have a retarding influence on the velocity of transformation, as was found by Reinders in the case of mercuric iodide.[1]

The velocity of transformation, also, is variously affected by different solvents, and in some cases, at least, it appears to be slower the more viscous the solvent ;[2] indeed, Kastle and Reed state that yellow crystals of mercuric iodide, which, ordinarily, change with considerable velocity into the red modification, have been preserved for more than a year under vaseline.

Change from the yellow to the red form of mercuric iodide at the ordinary temperature is retarded by the presence of mercuric chloride or bromide. Moreover, if mercuric iodide is heated to various temperatures above the melting-point, and then kept at the ordinary temperature, the velocity of change from yellow to red is all the greater the higher the temperature of heating.[3] It would appear that metastability is frequently if not always increased by the presence of impurities.[4]

Temperature, also, has a very considerable influence on the velocity of transformation. The higher the temperature, and the farther it is removed from the equilibrium point (transition point), the greater is the velocity of change. Above the transition point, these two factors act in the same direction, and the velocity of transformation will therefore go on increasing indefinitely the higher the temperature is raised. Below the transition point, however, the two factors act in opposite directions, and the more the temperature is lowered, the more is the effect of removal from the equilibrium point counteracted. A point will therefore be reached at which the velocity is a maximum. Reduction of the temperature below this point causes a rapid falling off in the velocity of change.[5] The point of maximum velocity, however, is not definite, but may be altered by various causes. Thus, Cohen found that in the case of tin, the point of maximum velocity was altered if the metal had already undergone transformation ; and also by the presence of different liquids.[6]

Lastly, the presence of small quantities of different substances—catalytic agents or catalysts—has a great influence on the velocity of

[1] *Z. physikal. Chem.*, 1899, **32**, 506. See also Chattaway and Lambert, *J. Chem. Soc.*, 1915, **107**, 1766.

[2] Kastle and Reed, *Amer. Chem. Jour.*, 1902, **27**, 209.

[3] Losana, *Gazzetta*, 1926, **56**, 301.

[4] Johnston, Merwin, and Williamson (*Amer. J. Sci.*, 1916 [4], **16**, 504) have pointed out that whereas natural calcite usually occurs in a very pure state, natural aragonite is contaminated by various impurities, such as the carbonates of lead, strontium, etc.

[5] See Lautz, *Z. physikal. Chem.*, 1913, **84**, 611. See also Bridgman, *Proc. Amer. Acad. Arts Sci.*, 1916, **52**, 57 ; Müller, *Z. physikal. Chem.*, 1914, **86**, 177.

[6] *Z. physikal. Chem.*, 1900, **35**, 581.

transformation. Thus, *e.g.* the conversion of white to violet phosphorus is accelerated by the presence of iodine (p. 59).

The occurrence of polymorphic forms and the persistence of the metastable state are facts of the highest practical and theoretical importance. In the case not only of tin, but also a number of other metals, *e.g.* bismuth, cadmium, copper, silver, and zinc, allotropic modifications exist with transition points at temperatures above the ordinary ; and, owing to the slowness of transformation, these metals exist, at the ordinary temperature, in a metastable state. On this fact depends the practical, everyday use of these metals.[1]

Recognition of the persistence of the metastable state is also, as Cohen more especially has emphasised, of the greatest importance in connection with the determination of the physical constants of the substances. Owing to the great slowness with which, in many cases, transformation of the metastable to the stable form takes place, great care must be exercised to ensure that one is dealing with a definite chemical individual and not with a mixture of polymorphs. Many determinations, indeed, of the physical properties of substances, found in the literature, are of doubtful value owing to insufficient care having been taken to ensure that the material used was a single crystalline form and not a variable mixture of two polymorphic forms.[2]

Metastability in Metals produced by Mechanical Stress.—It is well known that when copper, for example, is subjected to considerable mechanical stress, as when it is rolled, hammered, or drawn into wire, its physical properties undergo change. It becomes harder and less pliable, and its tensile strength increases. When, however, this hardened copper is heated to a temperature of about 300° it speedily becomes soft again and returns to its former state. A similar behaviour is found also in the case of other metals, such as gold, silver, platinum, and lead.

That a metal which has been subjected to considerable mechanical stress passes into a less stable form, is shown by the fact that the metal, after having been strained, possesses a higher solution pressure than the normal metal. That is to say, it acts as an anode to a piece of the normal metal when the two are placed in a solution of a salt of the metal.[3]

[1] See Cohen and Moesveld, *Z. physikal. Chem.*, 1913, **85,** 419 ; Cohen and Helderman, *ibid.*, 1914, **87,** 409, 419, 426 ; 1915, **89,** 493, 638, 728, 742 ; Cohen and Bosch, *ibid.*, 1915, **89,** 757 ; Heller, *ibid.*, 1915, **89,** 761 ; Cohen and Helderman, *ibid.*, 1910, **74,** 202 ; 1915, **89,** 733 ; Cohen, *ibid.*, 1914, **87,** 431 ; 1915, **89,** 489 ; Cohen and de Bruin, *ibid.*, 1915, **89,** 748 ; Cohen and Bruins, *ibid.*, 1920, **94,** 443 ; Cohen and Moesveld, *ibid.*, 1920, **95,** 285.

[2] Cohen, *Z. Elektrochem.*, 1925, **31,** 539 ; Cohen and Kooy, *Z. physikal. Chem.*, 1924, **109,** 81 ; Cohen and Moesveld, *ibid.*, p. 97 ; Cohen, Helderman and Moesveld, *ibid.*, p. 100 ; Cohen and Helderman, *ibid.*, 1924, **113,** 145 ; Cohen and Moesveld, *ibid.*, 1925, **115,** 151. See also Cohen, *Physico-chemical Metamorphosis and Problems in Piezochemistry* (1926).

[3] Hambuechen, *Electrometallurgist and Electrochemist*, 1902, **1,** 37 ; Spring, *Bull. Acad. Roy. Belg.*, Classe des Sciences, 1903, p. 1066 (see Cohen and Inouye, *Z. physikal. Chem.*, 1910, **71,** 301).

The change which occurs in the nature of the metal when mechanically worked has been studied by a number of investigators, and it has been found [1] that in the process of working, the metal crystals become more or less completely destroyed, and pass into an amorphous or quasi-amorphous state. A metal in such a state will therefore be related to the normal crystalline metal, in much the same way as superfused solid or glass is related to the stable crystalline form. Just as a metastable glass on being heated passes with greater or less velocity into the stable crystalline state ("devitrifies"), so the metastable, amorphous metal on being heated passes into the stable crystalline form; and the velocity of transformation will increase with elevation of temperature. At no point can there be a true equilibrium, and, consequently, contrary to the view expressed by some, there cannot be a definite transition point at which reciprocal transformation of one form into the other can occur.

In most cases the velocity of transformation of the metastable to the stable form takes place with very great slowness at the ordinary temperature, so that articles made of tin and other metals by rolling or moulding under pressure, may possess a considerable degree of permanence. It has, however, been observed by many investigators that a number of metals (*e.g.* tin, aluminium, lead) and alloys (*e.g.* brass, nickel-silver) which have been highly stressed by cold working, are liable to undergo what has been termed "season cracking." This behaviour, which is of much practical importance, is probably intimately connected with the production of an intercrystalline, metastable, vitreous phase.[2] The liability to season cracking can be diminished or removed by annealing.[3]

Law of Successive Reactions.—When sulphur vapour is cooled at the ordinary temperature, it first of all condenses to drops of liquid, which solidify in an amorphous form, and only after some time undergo crystallisation; or when phosphorus vapour is condensed, white phosphorus is first formed, and not the more stable form, violet phosphorus. It has also been observed that even at the ordinary temperature (therefore much below the transition point) sulphur may crystallise out from solution in benzene, alcohol, carbon disulphide, and other solvents, in the monoclinic form, the less stable crystals then undergoing transformation into the rhombic form; [4] a similar behaviour

[1] See, for example, Beilby, *Proc. Roy. Soc.*, 1902, **72**, 218; 1914, A., **89**, 593; *Aggregation and Flow of Solids* (Macmillan, 1921); Ewing and Rosenhain, *Phil. Trans.*, 1900, A., **193**, 353; compare Tammann, *Z. physikal. Chem.*, 1912, **80**, 687; Benedicks, *Revue de Métallurgie*, 1922, p. 505.

[2] Hatfield and Thirkell, *J. Inst. Met.*, 1919, **22**, 67; Moore, Beckinsale, and Mallinson, *ibid.*, 1921, **25**, 35; Cohen, *Z. physikal. Chem.*, 1909, **68**, 214; Cohen and Inouye, *ibid.*, 1910, **71**, 301; Cohen, *Trans. Faraday Soc.*, 1915, **10**, 216. A comprehensive discussion of the phenomenon of season cracking will be found in *Trans. Faraday Soc.*, 1921, **17**, Part I.

[3] Moore and Beckinsale, *J. Inst. Met.*, 1920, **23**, 225.

[4] Deville, *Compt. rend.*, 1852, **34**, 561; Payen, *ibid.*, 1852, **34**, 508; Debray, *ibid.*, 1858, **46**, 576. See also Frankenheim, *Pogg. Annalen*. 1836, **39**, 380; Bancroft, *J. Physical Chem.*, 1896, **1**, 142. It has also been found by Jaffé (*Z. physikal.*

has also been observed in the transformation of the monotropic crystalline forms of sulphur.[1]

Many other examples might be given. In organic chemistry, for instance, it is often found that when a substance is thrown out of solution, it is first deposited as a liquid, or as a less stable crystalline form, which passes later into the more stable crystalline form. In analysis, also, rapid precipitation from the concentrated solution often causes the separation of a less stable and more soluble amorphous form.

The prior formation of the less stable crystalline form can be well demonstrated by means of *p*-bromoacetanilide or by 2 : 4-dibromoacetanilide.[2] These compounds separate out from solution as needle-shaped crystals, forming a voluminous crystalline mass. When left in contact with the mother liquor, however, these crystals change, more or less rapidly, according to the solvent employed, into the more stable, compact crystalline form. The change in appearance is very marked, as is shown by the photographs (Fig. 10) of 2 : 4-dibromoacetanilide crystallised from alcoholic solution.[3]

Further, when a calcium salt is added to a solution of sodium potassium tartrate, the hydrate, $C\bar{a}\bar{T}$, $6H_2O$, separates out as needle-shaped crystals; and these then change into orthorhombic crystals of the more stable hydrate, $C\bar{a}\bar{T}$, $4H_2O$.[4]

On account of the great frequency with which the prior formation of the less stable form occurs, Ostwald [5] has put forward the *law of successive reactions*, which states that when a system passes from a less stable condition it does not pass directly into the most stable of the possible states; but into the next more stable, and so step by step into the most stable. This law explains the formation of the metastable forms of monotropic substances, which would otherwise not be obtainable. Although it is not always possible to observe the formation of the least stable form, it should be remembered that that may quite conceivably be due to the great velocity of transformation of the less stable into the more stable form. From what we have learned about the velocity of transformation of metastable phases, we can understand that rapid cooling to a low temperature will tend to preserve the less stable form; and, on account of the influence of temperature in in-

Chem., 1903, **43**, 465) that when spontaneous crystallisation from solution occurs, the less stable form always separates first when purification has been carried sufficiently far.

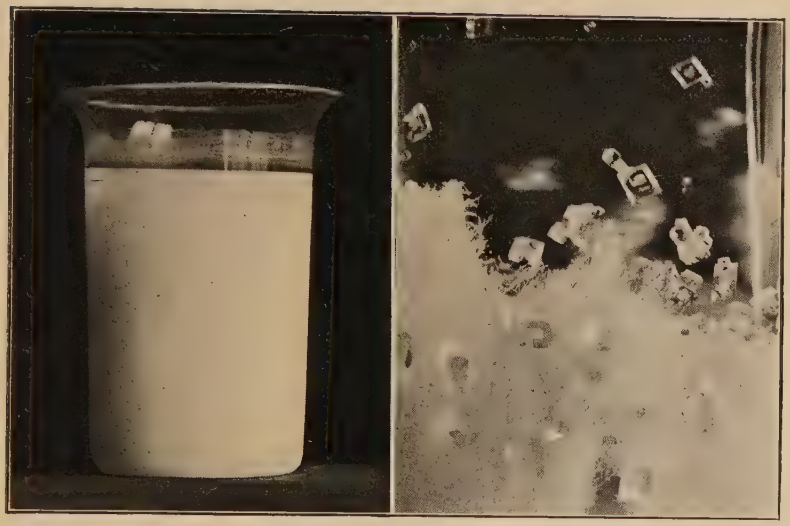
[1] Brauns, *Jahrb. Min. Beil.-Bd.*, 1899, **13**, 84.

[2] Chattaway and Lambert, *J. Chem. Soc.*, 1915, **107**, 1766.

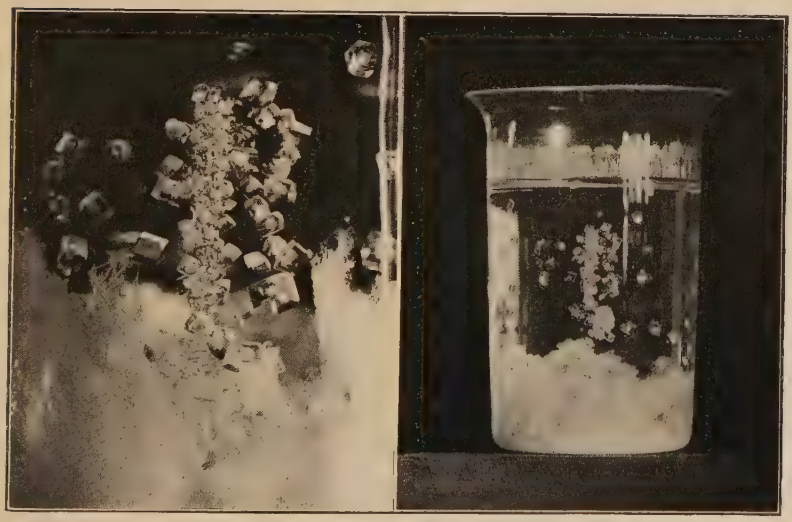
[3] For these photographs I am indebted to Dr. F. D. Chattaway. Transformation of the less stable needle-shaped crystals into the more stable compact crystals does not always take place spontaneously. Chattaway and Lambert state that needle-shaped crystals of 2 : 4-dibromoacetanilide in contact with alcoholic solution were kept for two years in a sealed tube, without transformation to the compact crystals taking place.

[4] Chattaway, *J. Amer. Chem. Soc.*, 1916, **38**, 2519.

[5] *Lehrbuch*, II., **2**, 445. See also *Principles of Inorganic Chemistry*, 4th edit., pp. 235 ff.



1 2



3 4

FIG. 10.—Crystallisation of 2 : 4-dibromoacetanilide. Photographs taken at intervals of two days.

[*To face page* 48.

creasing the velocity of change, it can be seen that the formation of the less stable form will be more difficult to observe in superheated than in supercooled systems. The factors, however, which affect the readiness with which the less stable modification is produced, appear to be rather various.[1]

Although a number of at least apparent exceptions to Ostwald's law have been found, it may nevertheless be accepted as a very useful generalisation which sums up very frequently observed phenomena.[2] Of these factors, the most important, according to Tammann,[3] is the readiness with which spontaneous formation of nuclei of the metastable and stable phases takes place in the supercooled system.

[1] Schaum and Schönbeck, *Annalen der Physik*, 1902 [4], **8**, 652. See also Chr. Füchtbauer, *Z. physikal. Chem.*, 1904, **48**, 549. An explanation of the law of successive reactions on the basis of his theory of allotropy has been given by Smits, *Z. physikal. Chem.*, 1913, **84**, 385; *The Theory of Allotropy* (1922), p. 98.

[2] See Skrabal, *Z. Elektrochem.*, 1908, **14**, 529; *Z. physikal. Chem.*, 1910, **73**, 171; Tammann, *Z. physikal. Chem.*, 1909, **69**, 569.

[3] *Z. physikal. Chem.*, 1898, **25**, 422; *States of Aggregation* (1926), p. 220.

CHAPTER IV.

EXPERIMENTAL INVESTIGATION OF TYPICAL SYSTEMS OF ONE COMPONENT.

In the present chapter will be discussed the experimental investigation of a number of systems of one component, the behaviour of which will illustrate the general principles of the Phase Rule considered in the preceding chapter.

A. Water.

We have already, in the preceding chapter, referred in passing to the sublimation, vaporisation, and fusion curves of the substance water, the arrangement of which at the triple S—L—V is represented diagrammatically in Fig. 11. The triple point, as we have seen, lies at a pressure of about 4·6 mm. of mercury and about + 0·008° C. The curves BO, OA, and OC are the sublimation, vaporisation, and fusion curves respectively. The fusion curve slopes towards the pressure axis, indicating that the melting-point of ice is lowered by increase of pressure. The dotted curve OA′ represents the metastable vaporisation curve for supercooled water. It is, of course, continuous with the curve OA.

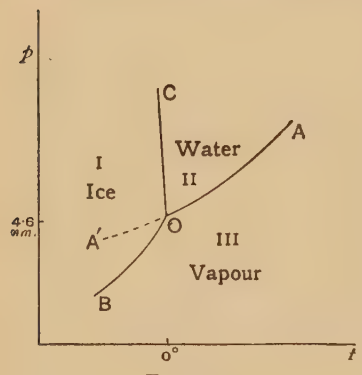


Fig. 11.

Other Systems of the Substance Water.—It was discovered by Tammann [1] that water can exist in other solid forms than that of ordinary ice; and the conditions under which these different solid phases can exist have been studied by him, and, more recently and fully, by P. W. Bridgman,[2] who carried his investigations up to a pressure of about 16,000 atmospheres. Although the two investigators are not in entire agreement with regard to the interpretation to be put

[1] *Annalen d. Physik*, 1900 [4], **2**, 1, 424; *Z. physikal. Chem.*, 1910, **72**, 609.
[2] *Z. anorgan. Chem.*, 1912, **77**, 377; *Proc. Amer. Acad.*, 1912, **47**, 441.

on the experimental results,[1] a brief summary of the relationships as they are interpreted by Bridgman may be given here, some of the results being represented graphically in Fig. 12.

According to the Phase Rule, each different variety of ice constitutes a separate phase and, consequently, it must be possible to obtain not only the ordinary triple point for solid—liquid—vapour which has already been described, but also other triple points at which the other forms of ice exist. Of such forms Bridgman has distinguished no fewer than four, besides ordinary ice, these different forms being designated ice I. (ordinary ice), ice II., ice III., ice V., ice VI. The existence and stability relations of another form, ice IV., discovered by Tammann, do not appear to be definitely settled.

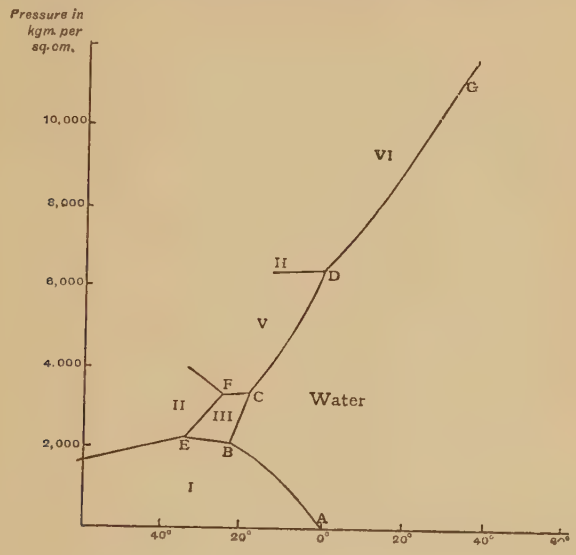


FIG. 12.

On investigating the equilibrium curve for ice I.—liquid, it is found that at a certain temperature and pressure, a second solid phase, ice III. is formed, giving rise to the invariant system ice I.—ice III.—liquid (Point B, Fig. 12).[2] Ice III. behaves differently from ice I. in that it expands on liquefying, and, consequently, its melting-point is raised by increase of pressure (curve BC). On following this curve to higher pressures and temperatures, another triple point (C) is reached at which ice V. coexists with ice III. and liquid. Similarly, one obtains

[1] Tammann, *Z. physikal. Chem.*, 1913, **84**, 257; Bridgman, *ibid.*, 1914, **86**, 513; Tammann, *ibid.*, 1914, **88**, 57.

[2] A similar triple point has been determined by Tammann in the case of phenol (*Annalen d. Physik*, 1902 [4], **9**, 249; *Kristallisieren und Schmelzen*, p. 308; *Z. physikal. Chem.*, 1911, **75**, 75). See also *Z. physikal. Chem.*, 1911, **75**, 733.

the curve CD for ice V. and liquid, and DG for ice VI. and liquid, D being a triple point for ice V.—ice VI.—liquid. The curve DG has been followed up to a pressure of about 16,000 atmospheres.

Besides the univariant curves for solid and liquid, one can also have univariant curves for two solid phases. Thus, BE represents the conditions of temperature and pressure for the coexistence of ice I. and ice III., while CF and DH refer to the systems ice III.—ice V., and ice V.—ice VI. respectively.

At the point E the solid phase ice II. is formed, giving rise to the triple point ice I.—ice II.—ice III. From this point there proceeds the curve EF for the system ice II.—ice III. Lastly, from E and F proceed two curves for the systems ice I.—ice II., and ice II.—ice V. respectively.

The different areas in Fig. 12, bounded by the curves for the univariant systems, represent the conditions for the stable existence of single phases, as represented in the diagram. From this diagram it is seen that the region of stability of ice III. is completely circumscribed.

In the following table are given the values of pressure and temperature corresponding with the different triple points as shown in Fig. 12.

Point.	System.	Temperature.	Pressure. Kgm. per sq. cm.
B	Ice I.—ice III.—liquid.	− 22·0°	2115
E	,, I.— ,, II.—ice III.	− 34·7°	2170
C	,, III.— ,, V.—liquid.	− 17·0°	3530
F	,, II — ,, III.—ice V.	− 24·3°	3510
D	,, V.— ,, VI.—liquid.	+ 0·16°	6380

The metastable continuation of the curve BE for ice I.—ice III. can be followed for a considerable distance into the field for ice II. The values for the curve BE and its metastable prolongation are given in the following table :—

Temperature.	Pressure. Kgm. per sq. cm.	$\frac{dp}{dT}$.	Δv.	q. cals. per gm.
− 20°	2103	− 5·3	0·1777	+ 5·6
− 30°	2156	− 3·2	0·1919	3·5
− 40°	2178	− 0·6	0·1992	0·7
− 50°	2160	2·0	0·2023	− 2·1
− 60°	2117	5·4	0·2049	− 5·5

The curve, in its metastable portion, passes through a point of maximum pressure $\left(\frac{dp}{dT} = 0\right)$ at − 43°. At this temperature the heat of transformation of ice I. into ice III. becomes zero.

B. Sulphur.

Sulphur exists in two well-known enantiotropic crystalline forms—rhombic and monoclinic. At the ordinary temperature, rhombic sulphur can exist unchanged, whereas, on being heated to temperatures somewhat below the melting-point, it passes into the monoclinic variety. On the other hand, at temperatures above 96°, monoclinic sulphur can remain unchanged, whereas at the ordinary temperature it passes slowly into the rhombic form.

If, now, we examine the case of sulphur with the help of the Phase Rule, we see that the following systems are theoretically possible :—

I. *Bivariant Systems : One component in one phase.*

(*a*) Rhombic sulphur.
(*b*) Monoclinic sulphur.
(*c*) Sulphur vapour.
(*d*) Liquid sulphur.

II. *Univariant Systems : One component in two phases.*

(*a*) Rhombic sulphur and vapour.
(*b*) Monoclinic sulphur and vapour.
(*c*) Rhombic sulphur and liquid.
(*d*) Monoclinic sulphur and liquid.
(*e*) Rhombic and monoclinic sulphur.
(*f*) Liquid and vapour.

III. *Invariant Systems : One component in three phases.*

(*a*) Rhombic and monoclinic sulphur and vapour.
(*b*) Rhombic sulphur, liquid and vapour.
(*c*) Monoclinic sulphur, liquid and vapour.
(*d*) Rhombic and monoclinic sulphur and liquid.

In Fig. 13 is represented the equilibrium diagram for these different systems of sulphur as determined by Tammann,[1] although, as more recent investigation has shown, the data on which the diagram was constructed are not quite accurate and take no consideration of the fact that sulphur exhibits dynamic allotropy and exists in different molecular species (p. 153). The diagram may, however, be taken as representing qualitatively the relations which exist. The more recent investigations of the melting-points of sulphur and of the equilibria which exist in molten sulphur will be discussed later (p. 153).

Point O (Fig. 13) is the triple point for rhombic sulphur—monoclinic sulphur—vapour, and is therefore the point of intersection of the three univariant curves, S_{rh}—V, S_{mon}—V, and S_{rh}—S_{mon}. At this triple point reversible transformation of rhombic and monoclinic sulphur can take place, these two forms of sulphur being enantiotropic.

[1] *Annalen d. Physik*, 1899 [3], **68**, 663.

Under atmospheric pressure, the transition point was found by Reicher[1] to lie at 95·5°. Rhombic sulphur is metastable above, and monoclinic sulphur is metastable below the transition point. Both forms, however, can be obtained in the metastable state, and transformation to the stable form may take place with great slowness (p. 46). The vapour pressure of sulphur between the temperatures of 50° and 210°

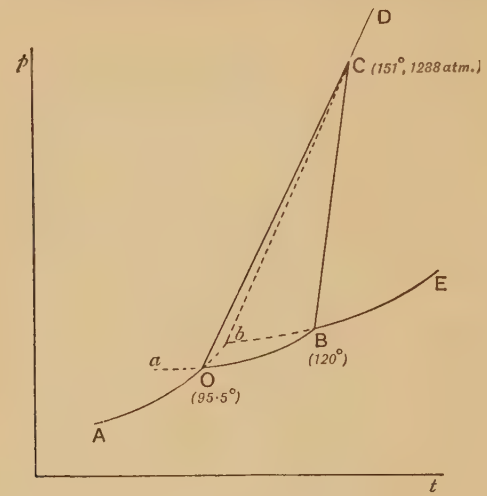


FIG. 13.

has been determined by Ruff and Graf.[2] The values obtained are given in the following table :—

VAPOUR PRESSURE OF SULPHUR.

Temperature.	Pressure in mm.	Temperature.	Pressure in mm.
49·7°	0·00034	131·9°	0·081
78·3°	0·0023	141°	0·131
89°	0·0057	147°	0·192
99·3°	0·0089	157°	0·332
104°	0·0115	162°	0·403
110·8°	0·0200	172°	0·629
114·5°	0·0285	189·5°	1·38
123·8°	0·0535	211·3°	3·14

[1] *Z. Kryst.*, 1884, **8**, 593. It has been shown that the transition temperature 95·5° refers to an equilibrium mixture of two molecular species, S_λ and S_μ (see p. 154). The transition point of rhombic sulphur, S_λ, free from S_μ, has been found by van Klooster to be 95·3° (see Kruyt, *Z. physikal. Chem.*, 1912, **81**, 726).

[2] *Z. anorgan. Chem.*, 1908, **58**, 209. See also Gruener, *J. Amer. Chem. Soc.*, 1907, **29**, 1396; Bodenstein, *Z. physikal. Chem.*, 1899, **30**, 118.

On plotting these numbers one obtains three curves of the type shown in Fig. 1 (p. 15), with points of intersection at about 92° (transition point) and 118° (melting-point). These curves are represented diagrammatically in Fig. 13 by AO, OB, BE.

Curve OC is the transition curve and represents the change of the transition point with pressure. Since the passage of the rhombic into monoclinic sulphur is accompanied by an increase of volume ($\Delta v = 0{\cdot}01395$ c.c. per gram), it follows from the theorem of Le Chatelier that the transition point is raised by increase of pressure. By means of this value of Δv and the heat of transformation, 3·12 cal. per gram, the value of $\frac{dT}{dp}$ can be calculated. Thus, for an increase of pressure of 1 atm. (1033·3 gm. per sq. cm.), we have

$$dT = \frac{368{\cdot}5 \times 0{\cdot}014 \times 1033}{3{\cdot}12 \times 42{,}670} = 0{\cdot}04°.$$

The transition point is raised 0·04° by an increase of pressure of 1 atm.[1]

At temperatures above 95·5°, monoclinic sulphur is the stable form. On being heated to 119·25° it melts.[2] This temperature may also be regarded as that of the triple point, S_{mon}—L—V (Point B, Fig. 13).

Since sulphur melts with increase of volume, the melting-point is raised by increase of pressure. The fusion curve BC, therefore, slopes to the right. The transition curve of rhombic and monoclinic sulphur, as we have seen, also slopes to the right, and more so than the fusion curve of monoclinic sulphur. There will, therefore, be a certain pressure and temperature at which the two curves will cut. This point lies at 151°, and a pressure of 1320 kilograms per sq. cm., or about 1288 atm.[3] It, therefore, forms another triple point, the existence of which had been predicted by Roozeboom,[4] at which rhombic and monoclinic sulphur are in equilibrium with liquid sulphur. It is represented in our diagram by the point C. *Beyond this point monoclinic sulphur ceases to exist in a stable condition.* At temperatures and pressures above this triple point, rhombic sulphur will be the stable modification, and this fact is of mineralogical interest, because it explains the occurrence in nature of well-formed rhombic crystals. Under ordinary conditions, monoclinic sulphur separates out on cooling fused sulphur, but at temperatures above 151° and under pressures greater than 1288 atm., the rhombic form would be produced.[5]

Metastable Systems.—On account of the slowness with which transformation of one crystalline form into the other takes place, it has been found possible to heat rhombic sulphur up to its melting-

[1] Tammann, *Annalen d. Physik*, 1899 [3], **68**, 629; Brönsted, *Z. physikal. Chem.*, 1906, **55**, 380.

[2] Smith and Holmes, *Z. physikal. Chem.*, 1903, **42**, 469. See also p. 155.

[3] Tammann, *Annalen d. Physik*, 1899 [3], **68**, 629.

[4] *Rec. Trav. Chim. Pays-Bas*, 1887, **6**, 314.

[5] Cf. van't Hoff, *Lectures on Physical Chemistry*, I., p. 27 (Arnold)

point, 112·8°. At this temperature, both rhombic sulphur and the liquid are metastable, the vapour pressure being greater than that of solid monoclinic sulphur. This point is represented in Fig. 13 by point *b*. From the diagram it is seen that the melting-point of the metastable is lower than that of the stable form.

Not only has the metastable melting-point of rhombic sulphur been determined, but the metastable fusion curve, *bC*, has also been obtained. This curve must pass through the triple point for rhombic

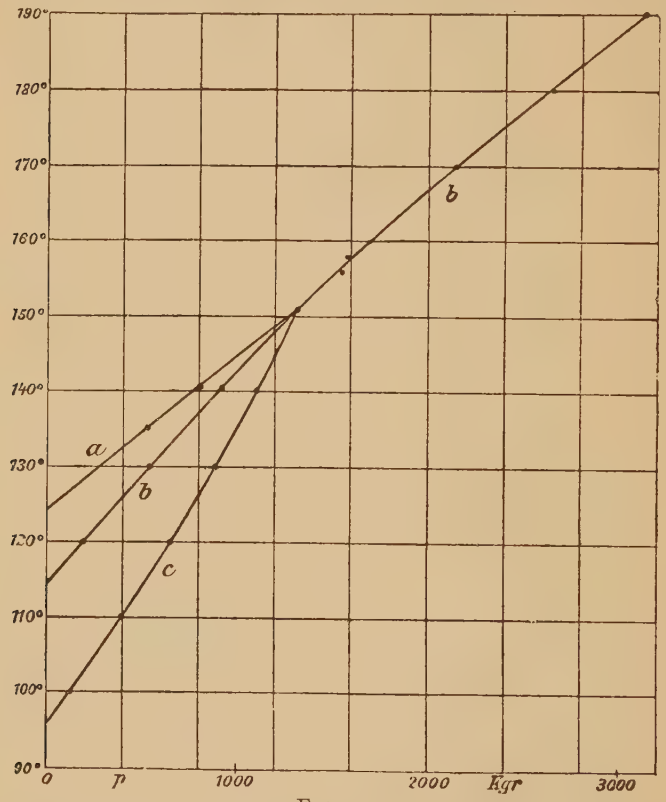


FIG. 14.

sulphur—monoclinic sulphur—liquid, and on passing this point it becomes a stable fusion curve. The continuation of this curve, therefore, above 151° forms the stable fusion curve of rhombic sulphur (curve CD).

These curves have been investigated at high pressures by Tammann, and the results are represented according to scale in Fig. 14,[1] *a* being the

[1] Tammann, *Annalen d. Physik*, 1899 [3], **68**, 629; *Kristallisieren und Schmelzen* (Barth, 1903). See also Rose and Mügge, *Nach. K. Ges. Wiss. Göttingen*, 1922, **10**, 105.

curve for monoclinic sulphur and liquid; *b*, that for rhombic sulphur and liquid; and *c*, that for rhombic and monoclinic sulphur. (In Fig. 14, the pressures are given as abscissæ and the temperatures as ordinates.)

Bivariant Systems.—Just as in the case of the diagram of states of water, the areas in Fig. 13 represent the conditions for the stable existence of the single phases: rhombic sulphur in the area to the left of AOCD; monoclinic sulphur in the area OBC; liquid sulphur in the area EBCD; sulphur vapour below the curves AOBE. As can be seen from the diagram, the existence of monoclinic sulphur is limited on all sides, its area being bounded by the curves OB, OC, BC. At any point outside this area, monoclinic sulphur can exist only in a metastable condition.

Other crystalline forms of sulphur have been obtained,[1] so that the existence of other systems of the one-component sulphur besides those already described is possible. Of these forms one may mention the readily obtainable but not very familiar mother-of-pearl sulphur or S_{III}.

To obtain this modification the discovery of which is due to Gernez,[2] molten sulphur, after being heated in a test-tube to above 150°, is cooled down to and maintained at a temperature of about 98° (*e.g.* in a water bath). On gently rubbing the inner walls of the tube with a glass rod, the sulphur crystallises in the nacreous form.[3] This form of sulphur is monotropic with respect to rhombic and monoclinic sulphur. At all temperatures up to its melting-point, 106·8°, mother-of-pearl sulphur is metastable.

C. Tin.

Another substance capable of existing in more than one crystalline form is the metal tin, and although the general behaviour, so far as studied, is analogous to that of sulphur, a short account of the two varieties of tin may be given here, not only on account of their metallurgical interest, but also on account of the importance which the phenomena possess for the employment of this metal in everyday life.

After a winter of extreme severity in Russia (1867-68), the somewhat unpleasant discovery was made that a number of blocks of tin, which had been stored in the Customs House at Petrograd (Leningrad), had undergone disintegration and crumbled to a grey powder.[4] That tin undergoes change on exposure to extreme cold was known, however, before that time, even as far back as the time of Aristotle, who spoke of the tin as "melting."[5] Ludicrous as that term may now

[1] Brauns, *Jahrb. Min. Beil.-Bd.*, 1899-1901, **13**, 39.
[2] *J. de Phys.*, 1884, **3**, 76.
[3] Smith and Carson, *Z. physikal. Chem.*, 1911, **77**, 661.
[4] Fritsche, *Ber.*, 1869, **2**, 112, 540.
[5] *De mirabilibus Auscultationibus*, Cap. 51 (*v.* Cohen, *Z. physikal. Chem.*, 1901, **36**, 513).

appear, Aristotle nevertheless unconsciously employed a strikingly accurate analogy, for the conditions under which ordinary white tin passes into the grey modification are, in many ways, quite analogous to those under which a substance passes from the solid to the liquid state. The knowledge of this was, however, beyond the wisdom of the Greek philosopher.

For many years there existed considerable confusion both as to the conditions under which the transformation of white tin into its allotropic modification occurs, and to the reason of the change. Under the guidance of the Phase Rule, however, the confusion which obtained has been cleared away, and the " mysterious " behaviour of tin brought into accord with other phenomena of transformation.[1]

Transition Point.—Just as in the case of sulphur, so also in the case of tin, there is a transition point above which the one form, ordinary white tin, and below which the other form, grey tin, is the stable variety. In the case of this metal, the transition point has been found by Cohen, who employed the dilatometric method (Appendix), to be 18°. Below this temperature, grey tin is the stable form. But, as we have seen in the case of sulphur, the change of the metastable into the stable solid phase occurs with considerable slowness, and this behaviour is found also in the case of tin. Were it not so, we should not be able to use this metal for the many purposes to which it is applied in everyday life ; for, with the exception of a comparatively short period in the year, the mean temperature of our climate is below 18°, and *white tin is, therefore, at the ordinary temperature, in a metastable condition.* The change, however, into the stable form at the ordinary temperature, although slow, nevertheless takes place, as is shown by the partial or entire conversion of articles of tin which have lain buried for several hundreds of years. Cases also are recorded of medals and other articles of tin, preserved in museums, which, even in a much shorter period, have suffered damage and disfigurement owing to the formation of wart-like patches of grey tin ; and tin organ pipes have become perforated and useless, even after the short space of seven years, owing to the spontaneous transformation of the less stable white into the more stable grey tin.[2]

On lowering the temperature, the velocity with which the transformation of the tin occurs is increased, and Cohen and van Eyk found that the temperature of maximum velocity is about — 50°. Contact with the stable form will, of course, facilitate the transformation.

The change of white tin into grey takes place also with increased velocity in presence of a solution of tin ammonium chloride (pink salt), which is able to dissolve small quantities of tin. In presence of such a solution, also it was found that the temperature at which the velocity of transformation was greatest was raised to 0°. At this temperature,

[1] E. Cohen and C. van Eyk, *Z. physikal. Chem.*, 1899, **30,** 601 ; Cohen. *ibid.*, 1900, **33,** 59 ; **35,** 588 ; 1901, **36,** 513 ; Cohen and E. Goldschmidt, *ibid.*, 1904, **50,** 225 ; Cohen, *ibid.*, 1908, **63,** 625.

[2] *Z. physikal. Chem.*, 1908, **63,** 625.

FIG. 15.—White tin passing into grey tin.

[*To face page* 59.

white tin, in contact with a solution of tin ammonium chloride and the grey modification, undergoes transformation to an appreciable extent in the course of a few days.

Fig. 15 is reproduced from a photograph of a piece of white tin undergoing transformation into the grey variety.[1] The bright surface of the tin becomes covered with a number of warty masses, formed of the less dense grey form, and the number and size of these continue to grow until the whole of the white tin has passed into a grey powder. On account of the appearance which is here seen, this transformation of tin has been called by Cohen the "tin plague."

Besides grey tin and white tin, the crystalline form of which is tetragonal, there exists a third or rhombic form which is stable above 202·8°.[2] The brittleness which is developed in tin when heated above about 200° is due to the change from the tetragonal to the rhombic form.

D. Phosphorus.

Phosphorus has long been known to exist in two distinct crystalline forms, white phosphorus belonging to the regular system, and red or violet [3] phosphorus belonging to the hexagonal system. When white phosphorus is heated, transformation into red or violet phosphorus takes place with appreciable velocity at temperatures above 260°, and the velocity of transformation increases as the temperature is raised. Even at lower temperatures the velocity of transformation is increased under the influence of light,[4] or by the presence of catalysts, such as iodine [5] and sodium.[6]

From determinations of the vapour pressures of liquid white phosphorus and of solid violet phosphorus,[7] it was found that the vapour

[1] *Z. physikal. Chem.*, 1900, **33**, 58.

[2] Smits and de Leeuw, *Proc. K. Akad. Wetensch. Amsterdam*, 1912, **15**, 676. See also Degens, *Z. anorgan. Chem.*, 1909, **63**, 207; Cohen, *Z. physikal. Chem.*, 1909, **68**, 214.

[3] The so-called red phosphorus, prepared by heating white phosphorus, varies in its properties (colour, vapour pressure, etc.) with the temperature to which and length of time during which it is heated. As the temperature is raised and the heating continued, the colour darkens to violet. A product with definite vapour pressure can be obtained by heating white phosphorus at about 550° for some hours. Sometimes the product is red and sometimes violet in colour, but the specific gravity (2·34) and the vapour pressure are the same (Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249). Owing to the variability of the different red forms of phosphorus, it is perhaps better to call the product having definite physical properties, violet phosphorus. It is identical with Hittorf's metallic phosphorus.

[4] Pedler, *J. Chem. Soc.*, 1890, **57**, 599. [5] Brodie, *ibid.*, 1853, **5**, 289.

[6] Bridgman, *J. Amer. Chem. Soc.*, 1916, **38**, 609.

[7] Smits and Bokhorst, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1174; 1914-15, **17**, 678, 962, 973; 1916, **18**, 106; *Z. physikal. Chem.*, 1916, **91**, 249. Compare Jolibois, *Compt. rend.*, 1909, **149**, 287; 1910, **151**, 382. The vapour pressure of liquid white phosphorus in the range of temperature 44°-150° has been determined by Macrae and Voorhis (*J. Amer. Chem. Soc.*, 1921, **43**, 547), and the values found can be represented by the expression $\log_{10} P$ (mm. Hg) = 7·9542 − 2757·5 T. The values obtained are much lower than those extrapolated from the vapour-pressure curve of Smits and Bokhorst.

pressure of the latter is considerably lower than that of the former at the same temperature, as is shown by the values given in the following tables :—

Vapour Pressure of Liquid White Phosphorus.

Temperature.	Pressure. Atm.	Temperature.	Pressure. Atm.	Temperature.	Pressure. Atm.
169°	0·04	229·8°	0·32	298·6°	1·38
181·3°	0·07	237·9°	0·42	331·8°	2·47
185·5°	0·09	252·0°	0·54	342·0°	2·95
206·9°	0·18	265·5°	0·74	355·7°	3·88
210·0°	0·20	280·5°	1·00	409·3°	7·36

Vapour Pressure of Violet Phosphorus.

Temperature.	Pressure. Atm.	Temperature.	Pressure. Atm.	Temperature.	Pressure. Atm.
308·5°	0·07	472·5°	3·88	581°	36·49
346°	0·13	486·5°	5·46	587·5°	41·77
379·5°	0·35	505°	8·67	588°	42·10
408·5°	0·79	515°	10·43	589·5°	43·1
433·5°	1·49	522°	11·61	(Triple point.)	
450·5°	2·30	561°	24·3		
463·5°	3·18	578°	34·35		

Throughout the whole range of temperature investigated, white phosphorus must be considered as the less stable (metastable) form, for although it can exist in contact with red (violet) phosphorus for a long period, its vapour pressure is greater than that of the latter, and transformation of the white into the red or violet modification takes place spontaneously. The solubility of white phosphorus in different solvents, moreover, is greater [1] than that of violet phosphorus ; and, as we shall find later, the solubility of the metastable form is always greater than that of the stable.

The vapour pressure of fused violet phosphorus has also been determined by Smits and Bokhorst [2] not only at temperatures above the triple point for solid—liquid—vapour, but also at temperatures considerably below this. The values found are contained in the following table :—

[1] This is a familiar fact in the case of the solubility in carbon disulphide.

[2] *Proc. K. Akad. Wetensch. Amsterdam*, 1914-15, **17**, 678, 962, 973. See also *Z. physikal. Chem.*, 1916, **91**, 249.

VAPOUR PRESSURE OF LIQUID VIOLET PHOSPHORUS.

Temperature.	Pressure. Atm.	Temperature.	Pressure. Atm.
504°	23·2	602°	47·0
550°	33·0	621°	53·9
569°	37·6	634°	58·6
581°	41·1		

Besides the ordinary white phosphorus which crystallises in the regular system, Bridgman [1] has discovered the existence of a second form of white phosphorus, possibly belonging to the hexagonal system. These two forms of white phosphorus are enantiotropic, with a transition point at — 76·9° under atmospheric pressure.

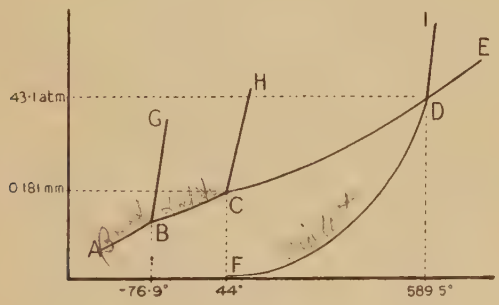


FIG. 16.

Taking into account the different facts set out above, we may represent the equilibrium conditions of the system phosphorus by the diagram,[2] Fig. 16.

In this figure FD represents the conditions of equilibrium of the univariant system, violet phosphorus and vapour, which ends at D, the triple point for solid—liquid—vapour, or the melting-point of violet phosphorus under the pressure of its own vapour. This point,

[1] *J. Amer. Chem. Soc.*, 1914, **36**, 1344.

[2] A number of facts lead to the view that in the case of phosphorus as in the case of sulphur, a condition of dynamic allotropy exists (Cohen and Olie, *Z. physikal. Chem.*, 1910, **71**, 1; Stock and Stamm, *Ber.*, 1913, **46**, 3497; Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249). The equilibrium relations would therefore be those of a pseudo-binary system or of a system of perhaps even higher order. For a discussion of the phosphorus systems from this point of view, see Smits, *Versl. K. Akad. Wetensch. Amsterdam*, 1912, **21**, 753; 1914, **22**, 1145; Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249.

according to Smits and Bokhorst,[1] lies at 589·5° and a pressure of 43·1 atm. According to Marckwald and Helmholz,[1] the melting-point is 592·5° ± 0·5°.

This triple point is the point of intersection of the three univariant systems solid—vapour (curve FD), liquid—vapour (curve DE), solid—liquid (curve DI). The values of the vapour pressures of solid and of liquid violet phosphorus are given in the tables on pp. 60 and 61. The curve DE will end abruptly at the critical point of liquid phosphorus. The critical temperature was found by W. A. Wahl [2] to lie at 695° C.; and from the course of the vapour-pressure curve, Smits and Bokhorst [3] have calculated that at this temperature the pressure (critical pressure) would be 82·2 atm. According to Marckwald and Helmholz, the critical temperature is 720·6°.

It has been found possible to follow the vaporisation curve of (supercooled) liquid phosphorus downwards to more than 80° below the triple point.

The course of the curve DI has not yet been determined, but from theoretical considerations (see p. 18), this curve must slope slightly to the right; that is, increase of pressure will raise the melting-point of violet phosphorus.

As has already been stated, two forms of white phosphorus are known which show a transition point under atmospheric pressure at − 76·9°. This is represented by the point B in the equilibrium diagram. This transition point is raised by pressure, as is shown by the following data determined by Bridgman :—

Pressure. Kgm. per sq. cm.	Temperature.	Pressure. Kgm. per sq. cm.	Temperature.
1	− 76·9°	9,000	32·7°
6000	− 2·4°	11,000	54·4°
8000	+ 21·4°	12,000	64·4°

Increase of pressure by 1 atm. raises the transition point by about 0·012°. The transition curve, BG, therefore, slopes away from the pressure axis.

When white phosphorus is heated to 44·1°, it melts.[4] At this

[1] Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249; Marckwald and Helmholz, *Z. anorgan. Chem.*, 1922, **124**, 81. Various values have been obtained for the melting-point of red (violet) phosphorus, varying from 597° to 630° (Chapman, *J. Chem. Soc.*, 1899, **75**, 734; Stock and Gomolka, *Ber.*, 1909, **42**, 4510; Stock and Stamm, *ibid.*, 1913, **46**, 3497).

[2] *Meddelanden fran Finska Kemist-Samfundet*, 1913, p. 3.

[3] *Z. physikal. Chem.*, 1916, **91**, 249.

[4] Smits and Bokhorst, *Z. physikal. Chem.*, 1914, **88**, 608. See also Smits and Leeuw, *ibid.*, 1911, **77**, 367; Boeseken, *Rec. trav. chim.*, 1907, **26**, 289; Macrae and Voorhis, *J. Amer. Chem. Soc.*, 1921, **43**, 547. The melting-point depends, according to Smits and Bokhorst, on the previous history of the phosphorus, a behaviour which has been interpreted by Smits as due to the production of a second molecular species (*Versl. K. Akad. Wetensch. Amsterdam*, 1915, **23**, 1403; Smits and Bokhorst, *Z. physikal. Chem.*, 1914, **88**, 608).

point, therefore, marked C in our diagram, we have another triple point, white phosphorus—liquid—vapour; the pressure at this point has been calculated to be 0·181 mm.[1] This point is the intersection of three curves, viz. the sublimation curve, vaporisation curve, and the fusion curve of white phosphorus. The fusion curve, CH, has been determined by Tammann [2] and by G. A. Hulett,[3] and it was found that increase of pressure by 1 atm. raises the melting-point by 0·029°. Some of the values obtained are as follows:—

Pressure in atm.	1	50	150	250	300
Melting-point	44·10°	45·50°	48·45°	51·33°	52·80°

From these data it follows that the melting-point curve, CH, slopes more to the right than does the transition curve, BG. The sublimation curves, AB and BC, for the two crystalline forms of white phosphorus, have not been determined.

As can be seen from the tables of vapour pressures (pp. 60 and 61), the vapour pressure of molten white phosphorus has been determined up to 409°, and that of molten violet phosphorus (supercooled) down to a temperature of 504°, leaving a gap of about 100° in which vapour pressures could not be determined. From the course of the two vapour-pressure curves, however, it is certain that we are dealing with two parts of a continuous vapour-pressure curve; [4] and we must therefore conclude that molten white phosphorus is supercooled violet phosphorus. The vapour pressure curve CDE is therefore continuous.

When white phosphorus is heated at 200° under a pressure of 12,000 kgm. per sq. cm., transformation takes place into another allotropic modification known as black phosphorus.[5] This forms a black crystalline solid, insoluble in carbon disulphide. It can be ignited with difficulty with a match, its ignition temperature in air being about 400°. When heated in a closed tube it vaporises and condenses to violet and white phosphorus. It differs from the other forms of phosphorus in being a conductor of electricity. Its density is 2·691. The question of the relative stability of violet and black phosphorus has perhaps not yet been definitely settled; [6] but the results obtained point to violet phosphorus being the more stable form.[7]

As compared with monotropic substances like benzophenone, phosphorus exhibits the peculiarity that transformation of the metastable into the stable modification takes place with great slowness; and further, the time required for the production of equilibrium between

[1] Macrae and Voorhis, *J. Amer. Chem. Soc.*, 1921, **43**, 547.
[2] *Annalen d. Physik*, 1898 [3], **66**, 492.
[3] *Z. physikal. Chem.*, 1899, **28**, 666.
[4] Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249.
[5] Bridgman, *J. Amer. Chem. Soc.*, 1914, **36**, 1344; 1916, **38**, 609. The existence of this form was predicted by Linck, *Z. anorgan. Chem.*, 1908, **56**, 393.
[6] Bridgman, *J. Amer. Chem. Soc.*, 1916, **38**, 609; Smits, Meyer and Beck, *Proc. K. Akad. Wetensch. Amsterdam*, 1916, **18**, 992.
[7] Smits, Meyer, and Beck, *Proc. K. Akad. Wetensch. Amsterdam*, 1918, **20**, 392; Marckwald and Helmholz, *Z. anorgan. Chem.*, 1922, **124**, 81.

red phosphorus and phosphorus vapour is great compared with that required for establishing the same equilibrium in the case of white phosphorus. This behaviour can be best explained by the assumption that change in the molecular complexity (polymerisation) occurs in the conversion of white into violet phosphorus, and when phosphorus passes into vapour (depolymerisation).[1] This is borne out by the fact that measurements of the vapour density of phosphorus vapour at temperatures of 500° and more show it to have the molecular weight represented by P_4,[2] and the same molecular weight has been found for phosphorus in solution.[3] On the other hand, it has been shown by R. Schenck,[4] that the molecular weight of violet phosphorus is at least P_8, and very possibly higher.

In the case of phosphorus, therefore, it is more than possible that we are dealing, not simply with two polymorphic forms of the same substance, but with polymeric forms, and that there is no transition point at temperatures above the absolute zero, unless we assume the molecular complexity of the two forms to become the same.[5] The curve for violet phosphorus would therefore lie below that of white phosphorus, for the vapour pressure of the polymeric form, if produced from the simpler form with evolution of heat, must be lower than that of the latter. As the vapour-pressure curve of molten white phosphorus is continuous with that of molten violet phosphorus, we must assume that in molten phosphorus we have an equilibrium between associated and non-associated molecules varying with the temperature.[6]

We have already seen in the case of water (p. 41) that the vapour pressure of supercooled water is greater than that of ice, and that therefore it is possible, theoretically at least, by a process of distillation, to transfer the water from one end of a closed tube to the other, and to condense it there as ice. On account of the very small difference between the vapour pressure of supercooled water and ice, this distillation process has not been experimentally realised. In the case of phosphorus, however, where the difference in the vapour pressures

[1] See Naumann, *Ber.*, 1872, **4**, 646; Troost and Hautefeuille, *Compt. rend.*, 1868, **66**, 795; 1868, **67**, 1345; Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249.

[2] Mitscherlich, *Annalen*, 1834, **12**, 137; Deville and Troost, *Compt. rend.*, 1863, **56**, 891.

[3] Beckmann, *Z. physikal. Chem.*, 1890, **5**, 79; Hertz, *ibid.*, **6**, 358.

[4] *Ber.*, 1902, **35**, 351. Cf. also K. Schaum, *Annalen*, 1898, **300**, 221; R. Wegscheider and Kaufler, *Sitzungsber. kaiserl. Akad. Wissensch. Wien*, 1901, **110**, II. 606. See also Boeseken, *Proc. K. Akad. Wetensch. Amsterdam*, 1907, **9**, 613.

[5] With regard to the nature of red phosphorus, see Cohen and Olie, jun., *Z. physikal. Chem.*, 1909, **71**, 1; Jolibois, *Compt. rend.*, 1910, **151**, 382; Stock and Stamm, *Ber.*, 1913, **46**, 3497; Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249.

[6] A discussion of the phosphorus equilibria from the point of view of the existence of dynamic allotropy in the liquid as well as in the solid phase is given by Smits, *Z. physikal. Chem.*, 1911, **76**, 439. For an experimental investigation of the relationships, see Smits and de Leeuw, *Z. physikal. Chem.*, 1911, **77**, 367; Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249. See also Marckwald and Helmholz, *Z. anorgan. Chem.*, 1922, **124**, 81.

is comparatively great, it has been found possible to distil white phosphorus from one part of a closed tube to another, and to condense it there as red phosphorus; and since the vapour pressure of red phosphorus at 350° is less than the vapour pressure of white phosphorus at 200°, it is possible to carry out the distillation from a *colder* part of the tube to a *hotter*, by having white phosphorus at the former and red phosphorus at the latter. Such a process of distillation has been carried out by Troost and Hautefeuille between 324° and 350°.[1]

E. Liquid Crystals or Anisotropic Liquids.

Phenomena Observed.—In 1888 it was discovered by Reinitzer [2] that the two substances, cholesteryl acetate and cholesteryl benzoate, possess the peculiar property of melting sharply at a definite temperature to milky liquids; and that the latter, on being further heated, suddenly become clear, also at a definite temperature. Other substances, more especially *p*-azoxyanisole and *p*-azoxyphenetole, were, later, found to possess the same property of having apparently a double melting-point.[3] On cooling the clear liquids, the reverse series of changes occurred.

The turbid liquids which were thus obtained were found to possess not only the usual properties of liquids (such as the property of flowing and of assuming a perfectly spherical shape when suspended in a liquid of the same density), but also those properties which had hitherto been observed only in the case of solid crystalline substances, viz. the property of double refraction and of giving interference colours when examined by polarised light; the turbid liquids are *anisotropic*. To such liquids, the optical properties of which were discovered by O. Lehmann, the name *liquid crystals*, or crystalline liquids, was given.[4] Since the term "crystal" implies the existence of a definite space lattice, which is not found in the case of "liquid crystals," it is perhaps better to use the term "anisotropic liquids."

Nature of Liquid Crystals.—The question as to the nature of liquid crystals has been the subject of prolonged discussion, and various attempts have been made to prove that the turbid liquids are in reality heterogeneous and are to be classed along with emulsions.[5] This view was no doubt largely suggested by the fact that the anisotropic liquids are turbid, whereas the "solid" crystals are clear. Lehmann found, however, that, when examined under the microscope, the "simple" liquid crystals are also clear, the apparent turbidity being due to the

[1] *Annales Chim. Phys.*, 1874 [5], **2**, 154.
[2] *Monatshefte*, 1888, **9**, 435.
[3] Gattermann, *Ber.*, 1890, **53**, 1738.
[4] *Z. physikal. Chem.*, 1889, **4**, 468; *Annalen d. Physik*, 1900 [4], **2**, 649.
[5] For a general discussion of liquid crystals, see Lehmann, *Flüssige Kristalle* (Engelmann), and *Die neue Welt der flüssigen Kristalle und deren Bedeutung für Physik, Chemie, Technik, und Biologie* (Engelmann); Schenck, *Kristallinische Flüssigkeiten und flüssige Kristalle* (Engelmann); Vorländer, *Kristallinisch-flüssige Substanzen* (Enke); Stumpf, *Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 1. A bibliography is given in the Fifth Edition of this book (1923).

aggregation of a number of differently oriented crystals, in the same way as a piece of marble does not appear transparent although composed of transparent crystals. Moreover, Vorländer and Kasten [1] have prepared crystalline (anisotropic) liquids which are quite clear and free from turbidity.

No proof of the heterogeneity of liquid crystals has been obtained, but rather all chemical and physical investigations indicate that they are homogeneous. No separation of a solid substance from the milky, anisotropic liquids has been effected; the anisotropic liquid is in some cases less viscous than the isotropic liquid formed at a higher temperature; and the temperature of liquefaction is constant, and is affected by pressure and admixture with foreign substances exactly as in the case of a pure substance.[2]

Recently, the structure of liquid crystals has been studied by van der Lingen [3] and by E. Hückel,[4] by the method of X-ray analysis. No evidence of any space-lattice structure, which is regarded as the criterion of a true crystal, was revealed in the first X-radiograms; but on further investigation of *p*-azoxyanisole in the liquid crystal form a pattern of faint horizontal lines was obtained. This might be interpreted as due to diffraction of the X-rays from parallel layers of lamellar molecules.

In view of the fact that Müller [5] has shown that the long molecules of such substances as stearic acid arrange themselves perpendicular to a layer of the substance, and in view, also, of the fact that Vorländer [6] has demonstrated that the property of forming liquid crystals is shown to the greatest extent by those molecules which contain long chains of atoms, it may be concluded that in liquid crystals we are dealing with a form of matter in which the molecules are neither unordered in their movement (isotropic liquid) nor arranged in a crystal lattice (crystalline solid), but are arranged parallelwise with one axis only fixed in space (Bose's "Swarm Theory").[7]

Equilibrium Relations in the Case of Liquid Crystals.—Whether we are dealing here with substances in two strictly crystalline and enantiotropic forms (which we may call the solid and liquid [8] crystalline forms), possessing a definite transition point, or whether we

[1] *Ber.*, 1908, **41**, 2033.
[2] A. C. de Kock, *Z. physikal. Chem.*, 1904, **43**, 129.
[3] *J. Franklin Inst.*, 1921, **191**, 651; 1921, **192**, 511.
[4] *Physikal. Z.*, 1921, **22**, 561. [5] *J. Chem. Soc.*, 1923, **123**, 2043.
[6] *Z. angew. Chem.*, 1922, **35**, 249. See also Vorländer, *Z. physikal. Chem.*, 1923, **105**, 211.
[7] *Physikal. Z.*, 1908, **9**, 708; 1909, **10**, 32, 230.
[8] On account of the fact that all grades of rigidity have been realised between the ordinary solid and the liquid state, in the case both of crystalline and of amorphous substances, it has been proposed to abandon the terms "solid" and "liquid," and to class bodies as "crystalline" or "amorphous," the passage from the one condition to the other being discontinuous; crystalline bodies possess a certain regular orientation of their molecules and a directive force, while in amorphous bodies these are wanting (see Lehmann, *Annalen d. Physik*, 1900 [4], **2**, 696). See, however, von Weimarn, *Kolloid Z.*, 1908, **3**, 282; 1909, **4**, 27, 123, 198, 252, 315; **5**, 62, 117, 150, 212; Doelter, *ibid.*, 1910, **7**, 29.

are dealing with an imperfectly crystalline, intermediate state of matter, which, however, possesses a certain stability and persistence throughout a certain range of temperature, we can represent the conditions of equilibrium by a diagram similar to that employed in the case of other enantiotropic substances, *e.g.* sulphur (p. 54).

In Fig. 17 there is given a diagrammatic representation of the relationships found in the case of *p*-azoxyanisole.[1]

Although the vapour pressure of the substance, in the solid or liquid state, has not been determined, it will be understood from what we have already learned, that the curves AO, OB, BC, representing the vapour pressure of solid crystals, liquid crystals, isotropic liquid, must have the relative positions shown in the diagram. Point O, the transition point of the solid into the liquid crystals, lies at 118·27°, and the change of the transition point with the pressure is + 0·032° for 1 atm. The transition curve OE slopes, therefore, slightly to the right. The point B, the melting-point of the liquid crystals, lies at 135·85°, and the melting-point is raised 0·0485° by increase of pressure of 1 atm. The curve BD, therefore, also slopes to the right, and more so than the transition curve. In this respect azoxyanisole is different from sulphur.

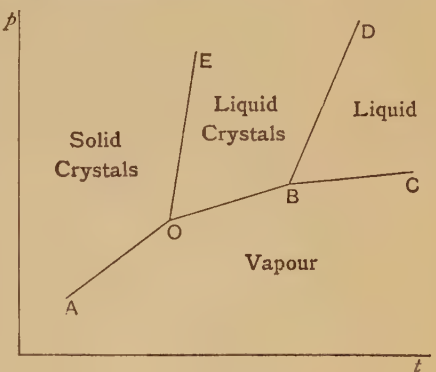


FIG. 17.

The areas bounded by the curves represent the conditions for the stable existence of the four single phases, solid crystals, liquid crystals, isotropic liquid, and vapour.

Some of the substances hitherto found to form liquid crystals are :—[2]

Substance.	Transition point.	Melting-point.
Cholesteryl benzoate	145·5°	178·5°
Azoxyanisole	118·3°	135·9°
Azoxyphenetole	134·5°	168·1°
Condensation product from benzaldehyde and benzidine	234°	260°
Azine of *p*-oxyethylbenzaldehyde	172°	196°
Condensation product from *p*-tolylaldehyde and benzidine	231°	—
p-Methoxycinnamic acid	169°	185°

[1] Hulett, *Z. physikal. Chem.*, 1899, **28**, 629.

[2] Schenck, *Kristallinische Flüssigkeiten und flüssige Kristalle*, p. 8 (Engelmann 1905); Vorländer, *Kristallinisch-flüssige Substanzen* (Enke); also Vorländer, *Ber.*, 1906, **39**, 803; 1907, **40**, 1415; 1908, **41**, 2033; *Z. angew. Chem.*, 1922, **35**, 249.

CHAPTER V.

SYSTEMS OF TWO COMPONENTS.

In the preceding pages there has been studied the behaviour of systems consisting of only one component, or systems in which all the phases, whether solid, liquid, or vapour, have the same chemical composition (p. 9). In some cases, as, for example, in the case of phosphorus and sulphur, the component was an elementary substance; in other cases, however, *e.g.* water, the component was a compound. The systems which we now proceed to study are characterised by the fact that the different phases have no longer all the same chemical composition, and cannot, therefore, according to definition, be considered as one-component systems.

In most cases, little or no difficulty will be experienced in deciding as to the *number* of the components, if the rules given on pp. 8 and 9 are borne in mind. If the composition of all the phases, each regarded as a whole, is the same, the system is to be regarded as of the first order, or a one-component system; if the composition of the different phases varies, the system must contain more than one component. If, in order to *express* the composition of all the phases present when the system is in equilibrium, two of the constituents participating in the equilibrium are necessary and sufficient, the system is one of two components. Which two of the possible substances are to be regarded as components will, however, be to a certain extent a matter of arbitrary choice.

The principles affecting the choice of components will best be learned by a study of the examples to be discussed in the sequel.

Different Systems of Two Components.—Applying the Phase Rule

$$F = n + 2 - r$$

to systems of two components ($n = 2$), we see that in order that the system may be invariant, there must be four phases in equilibrium together. Two components in three phases constitute a univariant, two components in two phases a bivariant system. In the case of systems of one component, the highest degree of variability found was two (one component in one phase); but, as is evident from the formula, there is a higher degree of freedom possible in the case of two-component systems. Two components existing in only one phase constitute a tervariant system, or a system with three degrees of freedom.

In addition to the pressure and temperature, therefore, a third variable factor must be chosen, and as such there is taken the *concentration of the components*. In systems of two components, therefore, not only may there be change of pressure and temperature, as in the case of one-component systems, but the concentration of the components in the different phases, or the composition of the phases, may also alter; a variation which did not require to be considered in the case of one-component systems.

Since a two-component system may undergo three possible independent variations, we should require for the graphic representation of all the possible conditions of equilibrium a system of three co-ordinates in space, three axes being chosen, say, at right angles to one another, and representing the three variables—pressure, temperature, and concentration of components (Fig. 18). A curve (*e.g.* AB) in the plane containing the pressure and temperature axes will then represent

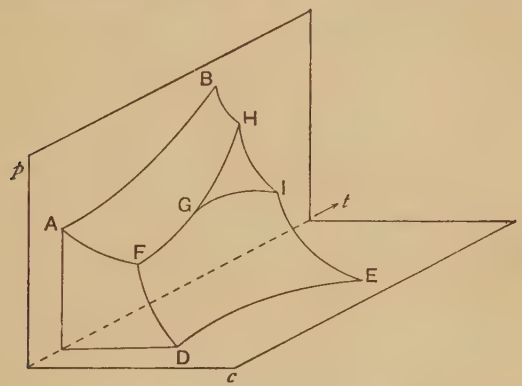


FIG. 18.

the relationship between pressure and temperature, the concentration remaining unaltered (*pt*-diagram); one in the plane containing the pressure and concentration axes (*e.g.* AF or DF), the change of pressure with the concentration, the temperature remaining constant (*pc*-diagram),[1] while in the plane containing the concentration and the temperature axes, the simultaneous change of these two factors at constant pressure will be represented (*tc*-diagram).[2] Any line (*e.g.* FG, or GH, or GI) situated in the space within the two planes, will represent the simultaneous variation of the three factors—pressure, temperature, concentration. Although we shall at a later point make some use of these solid figures, we shall for the most part consider, in any given case, the variation of only two of the variables pressure,

[1] Referred to also as the *px*-diagram, where *x* is the relative amount of one of the components.

[2] Also called the *tx*-diagram.

temperature and concentration, and shall employ, therefore, the simpler plane diagram.

The number of different systems which can be formed from two components, as well as the number of the different phenomena which can there be observed, is much greater than in the case of one component. In the case of no two substances, however, have all the possible relationships been studied; so that for the purpose of gaining an insight into the varied behaviour of two-component systems, a number of different examples will be discussed, each of which will serve to give a picture of some of the relationships.

Although the strict classification of the different systems according to the Phase Rule would be based on the variability of the systems, the study of the many different phenomena, and the correlation of the comparatively large number of different systems, will probably be rendered easiest by grouping these different phenomena into classes, each of these classes being studied with the help of one or more typical examples. The order of treatment adopted here is, of course, quite arbitrary; but has been selected from considerations of simplicity and clearness.

Classification and Order of Treatment.

For the discussion of the equilibria occurring in two-component systems, the following classification of systems, which also gives the order in which they will be discussed, has been adopted :—

A. Solid and gas phases only.
B. Two liquid phases only.
C. Solid and liquid phases only.
    I. The components are completely miscible in the liquid state.
        (*a*) The pure components only exist as solid phases.
        (*b*) Compounds are formed with a congruent melting-point.
        (*c*) Compounds are formed with an incongruent melting-point.
        (*d*) Solid solutions or mixed crystals are formed.
    II. The components are not completely miscible in the liquid state.
    III. Dynamic allotropy and pseudo-binary systems.
D. Solid, liquid, and gas phases coexist.
        (*a*) Only one of the components is volatile.
        (*b*) Both components are volatile.

Solutions.—In the case of the equilibria studied in the previous chapters, the different phases consisted of a single substance of definite composition or a definite chemical individual.[1]

[1] A chemical individual is a substance which persists as a phase of constant composition when the conditions of temperature, pressure, and composition of the other phases present undergo continuous alteration within certain limits—the limits of existence of the substance (Wald, *Z. physikal. Chem.*, 1897, **24**, 648).

But this invariability of the composition is by no means imposed by the Phase Rule ; on the contrary, it will be found that in the equilibria now to be studied the participation of phases of variable composition is in no way excluded. To such phases of variable composition there is applied the term *solution*. A solution, therefore, is to be defined as *a homogeneous mixture, the composition of which can undergo continuous variation within certain limits ;* the limits, namely, of its existence.[1] A solution, since it is a *homogeneous* mixture, constitutes a single phase.

It will be understood from the definition just given that the term solution is not restricted to any particular physical state of substances, but includes within its range not only the liquid, but also the gaseous and solid states. We may therefore have solutions of gases in liquids, and of gases in solids ; of liquids in liquids or in solids ; of solids in liquids, or of solids in solids. Solutions of gases in gases are, of course, also possible ; since, however, gas solutions never give rise to more than one phase, their treatment does not come within the scope of the Phase Rule, which deals with heterogeneous equilibria.

It should also be emphasised that the definition of solution given above neither creates nor recognises any distinction between solvent and dissolved substance (solute) ; and, indeed, a too persistent use of these terms and the attempt permanently to label the one or other of two components as the solvent or the solute, can only obscure the true relationships and aggravate the difficulty of their interpretation. In all cases it should be remembered that one is dealing with equilibria between two components (we confine our attention in the first instance to such), the solution being constituted of these components in variable and varying amounts. The change from the case where the one component is in great excess (ordinarily called the solvent) to that in which the other component predominates, may be quite gradual, so that it is difficult or impossible to say at what point the one component ceases to be the solvent and becomes the solute. The adoption of this standpoint need not, however, preclude one from employing the conventional terms solvent and solute in ordinary language, especially when reference is made only to some particular condition of equilibrium of the system, when the concentration of the two components in the solution is widely different.

[1] Van't Hoff, *Z. physikal. Chem.*, 1890, **5**, 323.

CHAPTER VI.

SYSTEMS OF TWO COMPONENTS (*Continued*).

A. Systems Consisting of Solid and Gas Phases only. Phenomena of Dissociation.

In dealing with two-component systems consisting of solid and gas phases only, the following chief cases call for mention :—

I. *The two components are gases and combine to form a dissociating solid.*

When ammonia and hydrogen chloride are brought together, combination takes place with formation of solid ammonium chloride. The systems are bivariant.

II. *One component is a gas and the other component is a solid.*

(*a*) *The gas is not absorbed by the solid component, but when the pressure reaches a certain value, combination of the two components can result.*

The graphic representation of such a system is shown in Fig. 19, the ordinates being the pressures of the gas and the abscissæ the concentration of the gaseous component in the solid phases. When the pressure of the gaseous component in contact with the solid component is continuously increased at constant temperature, the concentration of the gaseous component in the solid phase remains zero (since it is assumed that the gas does not dissolve in or is not absorbed by the solid component), until the pressure has increased to the point A. At this point, combination can take place. There will now be three phases present, namely, solid component, compound of the components, and gas. The system is therefore univariant, and if the temperature is maintained constant, the gas pressure will be constant, irrespective of the amount of compound formed, *i.e.* irrespective of the amount of the gaseous component in the two solid phases. This is indicated by the line AB. When the solid component has entirely disappeared, through combination with the gaseous component, the system ceases to be univariant; and if no absorption occurs, the pressure will again rise, as shown by the line BC. If a second compound can be formed, then a second pc-line will be obtained, similar to the preceding.

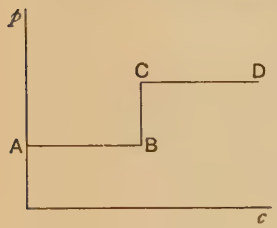


Fig. 19.

(*b*) *The gas is absorbed by the solid component and no compound is formed.*

If absorption of the gas by the solid component takes place with formation of a solid solution, then, as the system consists of only two phases, solution—vapour, it is bivariant. At constant temperature, therefore, the pressure will vary continuously with the concentration of the gas in the solid solution.

(*c*) *The gas is absorbed by the solid component and may also form a compound.*

When the gas is absorbed by the solid component, the pressure will, at constant temperature, vary continuously with the concentration of the gas in the solid solution as represented by the curve AB in Fig. 20. When, however, the pressure of the gas reaches a certain value, combination takes place; and since there are now three phases present, the system is univariant. At constant temperature, therefore, the pressure remains constant, as shown by the line BC in Fig. 20.

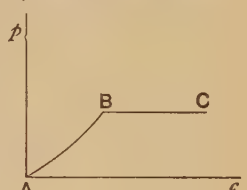


FIG. 20.

(*d*) *Absorption of gas occurs, and at a certain concentration the solid solution separates into two partially miscible solid solutions.*

When two partially miscible solid solutions are formed there will be three phases present, and the system will be univariant. At constant temperature the *pc*-curve will be a straight line, as in the case of the formation of a compound. The behaviour of this system will, therefore, also be represented diagrammatically by Fig. 20.

I. TWO GASEOUS COMPONENTS.

On being heated, ammonium chloride dissociates into ammonia and hydrogen chloride. Since, in this case, the vapour phase has the same total composition as the solid phase, viz. $NH_3 + HCl = NH_4Cl$, the system consists of only one component existing in two phases; it is therefore univariant, and to each temperature there will correspond a definite vapour pressure (dissociation pressure).[1] If, however, excess of one of the products of dissociation be added, the system becomes one of two components.

In the first place, analysis of each of the two phases yields as the composition of each, solid: $NH_4Cl(= NH_3 + HCl)$; vapour: $mNH_3 + nHCl$. Obviously the smallest number of substances by which the composition of the two phases can be expressed is two; that is, the number of components is two. What, then, are the components? The choice lies between $NH_3 + HCl$, $NH_4Cl + NH_3$ and $NH_4Cl + HCl$; for the three substances, ammonium chloride, ammonia, hydrogen chloride, are the only ones taking part in the equilibrium of the system.

[1] Ramsay and Young, *Phil. Trans.*, 1886, **177**, 87.

Of these three pairs of components, we should obviously choose as the most simple NH_3 and HCl, for we can then represent the composition of the two phases as the *sum* of the two components. If one of the other two possible pairs of components be chosen, we should have to introduce negative quantities of one of the components, in order to represent the composition of the vapour phase. Although it must be allowed that the introduction of negative quantities of a component in such cases is quite permissible, still it will be better to adopt the simpler and more direct choice, whereby the composition of each of the phases is represented as a sum of two components in varying proportions (p. 9).

If, therefore, we have a solid substance, such as ammonium chloride, which dissociates on volatilisation, and if the products of dissociation are added in varying amounts to the system, we shall have, in the sense of the Phase Rule, a *two-component system existing in two phases*. Such a system will possess two degrees of freedom. At any given temperature, not only the pressure, but also the composition, of the vapour phase, *i.e.* the concentration of the components, can vary. Only after one of these independent variables, *e.g.* the composition, has been arbitrarily fixed does the system become univariant, and exhibit a definite, constant pressure at a given temperature.

Now, although the Phase Rule informs us that at a given temperature change of composition of the vapour phase will be accompanied by change of pressure, it does not cast any light on the relation between these two variables. This relationship, however, can be calculated theoretically by means of the Law of Mass Action.[1] From this we learn that in the case of a substance which dissociates into equivalent quantities of two gases, the product of the partial pressures of the gases is constant at a given temperature.

This has been proved experimentally in the case of ammonium hydrosulphide, ammonium cyanide, phosphonium bromide, and other substances.[2]

II. (*a*) A Gaseous and a Solid Component which can form Compounds.

As an example of this, we may first consider the system formed by the two components CaO and CO_2, which can combine to form the compound $CaCO_3$. This substance, on being heated, dissociates into calcium oxide and carbon dioxide, and gives rise to the equilibrium $CaCO_3 \rightleftarrows CaO + CO_2$. In accordance with the definition given on p. 6, there are present here two solid phases, the carbonate and the quicklime, and one vapour phase; the system is therefore univariant. To each temperature, therefore, there will correspond a certain definite maximum pressure of carbon dioxide (dissociation pressure) and this

[1] See volume in this series on *Chemical Dynamics*, by J. W. Mellor.

[2] Isambert, *Compt. rend.*, 1881, **92**, 919; 1882, **94**, 958; 1883, **96**, 643. Walker and Lumsden, *J. Chem. Soc.*, 1897, **71**, 428.

will follow the same general law as the vapour pressure of a pure liquid (pp. 15 and 16). More particularly, it will be independent of the relative or absolute amounts of the two solid phases, and of the volume of the vapour phase. If the temperature is maintained constant, increase of volume will cause the dissociation of a further amount of the carbonate until the pressure again reaches its maximum value corresponding to the given temperature. Diminution of volume, on the other hand, will bring about the combination of a certain quantity of the carbon dioxide with the calcium oxide until the pressure again reaches its original value.[1]

The dissociation pressure of calcium carbonate was studied first by Debray,[2] and later by Le Chatelier,[3] but the determinations of these investigators cannot be regarded as trustworthy. More recently, the dissociation pressures of calcium carbonate have been investigated by Pott,[4] Zavrieff,[5] and Johnston,[6] and the values obtained by the last-mentioned, which have been confirmed by Jolibois and Bouvier,[7] may be accepted as the most accurate. The experimental numbers were found to be in close agreement with the equation

$$\log p = -9340/T + 1{\cdot}1 \log T - 0{\cdot}0012T + 8{\cdot}882,$$

and the numbers given in the following table have been calculated by means of this expression :—

Temperature.	Pressure in mm. of mercury.
500°	0·11
550°	0·57
600°	2·35
650°	8·2
700°	25·3
750°	68
800°	168
850°	373
900°	773
950°	1490
1000°	2710

The temperature at which the dissociation pressure is equal to 1 atm., is 898°. In a vessel open to the air, therefore, the complete decomposition of the calcium carbonate would not take place below this temperature by the mere heating of the carbonate. If, however, the carbon dioxide is removed as quickly as it is formed, say by a

[1] See Sosman, Hostetter, and Merwin, *J. Washington Acad. Sci.*, 1915, **5**, 563; Jolibois and Bouvier, *Compt. rend.*, 1921, **172**, 1182.

[2] *Compt. rend.*, 1867, **64**, 603. [3] *Ibid.*, 1883, **102**, 1243.

[4] Inaugural Dissertation, Freiburg i. Baden, 1905. See Riesenfeld, *J. Chim. phys.*, 1909, **7**, 561.

[5] *J. Chim. phys.*, 1909, **7**, 31. [6] *J. Amer. Chem. Soc.*, 1910, **32**, 938.

[7] *Compt. rend.*, 1921, **172**, 1182.

current of air, the entire decomposition can be made to take place at a much lower temperature. For the dissociation equilibrium of the carbonate depends only on the partial pressure of the carbon dioxide, and if this is kept small, then the decomposition can proceed, even at temperatures at which the pressure of the carbon dioxide is less than atmospheric pressure.

The dissociation pressures of calcium carbonate up to 1390° have also been determined by Smyth and Adams,[1] who find that the equation, $\log p = -11355/T - 5{\cdot}388 \log T + 29{\cdot}119$, gives values which are in harmony with their own and with Johnston's determinations. Somewhat higher values for the dissociation pressure (1 atm. at 882°) have, however, been obtained by Andrusov.[2]

Cadmium carbonate behaves similarly to calcium carbonate and, on being heated, gives rise to the equilibrium $CdCO_3 \rightleftharpoons CdO + CO_2$. The equilibrium pressure at different temperatures has been determined by Centnerszwer and Andrusov,[3] who find that the dissociation pressures are expressed by the formula $\log p = -12{\cdot}44 + 0{\cdot}02439\ T$. The reaction $CdO + CO_2 \rightarrow CdCO_3$ takes place about fifty times more slowly than the reaction $CdCO_3 \rightarrow CdO + CO_2$.

In the case of the systems $CaO—CO_2$ and $CdO—CO_2$, only one compound is formed by the components, and only two solid phases, therefore, are possible.[4] In many cases, however, more than one dissociating compound can be formed between a solid and a gaseous component, and two or more stable univariant systems may therefore be produced consisting of two solid phases and one gas phase. The behaviour which is found in such cases will best be understood by the consideration of definite systems which have been investigated experimentally.

Ammonia Compounds of Metal Chlorides.—Ammonia possesses the property of combining with various substances, chiefly the halides of metals, to form compounds which again yield up the ammonia on being heated. Thus, for example, on passing ammonia over silver chloride, absorption of the gas takes place with formation of the compounds $AgCl \cdot NH_3$, $2AgCl \cdot 3NH_3$ and $AgCl \cdot 3NH_3$, according to the conditions of the experiment. These were the first known substances belonging to this class, and were employed by Faraday in his experiments on the liquefaction of ammonia. Similar compounds have also been obtained by the action of ammonia on silver bromide, iodide, cyanide, and nitrate, and on the halogen compounds of calcium, zinc, magnesium and other metals. The behaviour of the ammonia compounds of silver chloride is typical of the compounds of this class, and may be briefly considered here.

The equilibria in the two-component system $AgCl—NH_3$ have been

[1] *J. Amer. Chem. Soc.*, 1923, **45**, 1167.
[2] *Z. physikal. Chem.*, 1925, **116**, 81.
[3] *Ibid.*, 1924, **111**, 79; *Acta Univ. Latviensis*, 1924, **10**, 495.
[4] If one excludes for the moment the possibility of polymorphism in the case of the compound.

most fully investigated by Biltz and Stollenwerk,[1] who have established the existence of the three compounds $AgCl \cdot 3NH_3$, $2AgCl \cdot 3NH_3$ and $AgCl \cdot NH_3$. On being heated, these compounds decompose and give rise to the equilibria :—

$$2(AgCl \cdot 3NH_3) \rightleftharpoons 2AgCl \cdot 3NH_3 + 3NH_3.$$
$$2AgCl \cdot 3NH_3 \rightleftharpoons 2(AgCl \cdot NH_3) + NH_3.$$
$$AgCl \cdot NH_3 \rightleftharpoons AgCl + NH_3.$$

In each case, therefore, there are three phases present, two solid phases and one gas phase. The systems are, therefore, univariant and to each temperature there must correspond a definite pressure of dissociation, quite irrespective of the amounts of the phases present. The values of these dissociation pressures are given in the following tables :—[2]

$2(AgCl \cdot 3NH_3) \rightleftharpoons 2AgCl \cdot 3NH_3 + 3NH_3$.		$2AgCl \cdot 3NH_3 \rightleftharpoons 2(AgCl \cdot NH_3) + NH_3$.	
Temperature.	Pressure in mm.	Temperature.	Pressure in mm.
− 25°	56·5	0°	42
− 16°	84	5·0°	55
0°	271	16·3°	116
+ 9·5°	464	19·0°	159
+ 14·0°	632	26·0°	231
+ 16·3°	701	32·8°	366

$AgCl \cdot NH_3 \rightleftharpoons AgCl + NH_3$.	
Temperature.	Pressure in mm.
0°	17
16·3°	42
32·8°	118
42°	240
43°	252
59°	613
63°	653

Since the dissociation pressure of the triammonia mono-chloride becomes equal to atmospheric pressure at a temperature of about 20°, this compound cannot be formed at temperatures above 20° by the passage of ammonia at atmospheric pressure over silver chloride. The

[1] *Z. anorgan. Chem.*, 1920, **114**, 174.

[2] See also Isambert, *Compt. rend.*, 1868, **66**, 1259; Horstmann, *Ber.*, 1876, **9**, 749; Jarry, *Annales Chim. Phys.*, 1899 [7], **17**, 327. To these dissociation pressure curves we may apply the formula $\frac{d \log_e p}{dT} = \frac{Q}{RT^2}$ (p. 19). See Bonnefoi, *Annales Chim. Phys.*, 1901 [7], **23**, 330; Horstmann, *Ber.*, 1881, **15**, 1242.

triammonia di-chloride, however, can be formed, for at this temperature its dissociation pressure amounts to only about 160 mm.

Emphasis may again be laid on the fact that *two* solid phases are necessary in order that the dissociation pressure at a given temperature shall be definite; *and for the exact definition of this pressure it is necessary to know, not merely what is the substance undergoing dissociation, but also what is the solid product of dissociation formed.* For the definition of the equilibrium, the latter is as important as the former. We shall presently find proof of this in the case of an analogous class of phenomena, viz. the dissociation of salt hydrates.

The behaviour which is observed when ammonia is withdrawn from or added to the system AgCl—NH_3 at constant temperature is of interest and importance. If, at constant temperature, the volume of the system is increased, or, if the ammonia which is evolved is pumped off, the pressure will remain constant so long as two solid phases are present, *i.e.* until the compound richer in ammonia is completely decomposed. There will then ensue a sudden fall in the pressure to the value appropriate to the next system of lower ammonia content. On continually withdrawing ammonia at constant temperature, therefore, there will be a step-wise diminution of the ammonia pressure.

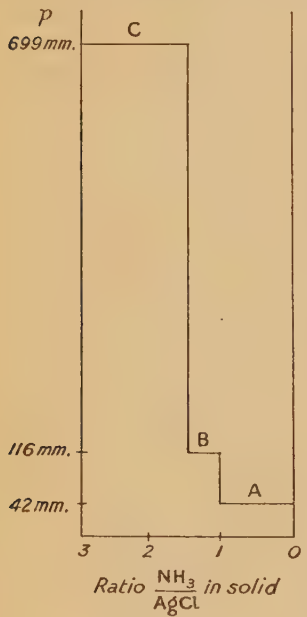


FIG. 21.

The reverse changes take place when the pressure of the ammonia is gradually increased. If ammonia is passed into a vacuous vessel containing silver chloride at a suitable and constant temperature, the pressure will increase until it has reached a certain value; the compound AgCl . NH_3 is then formed, and the pressure will now remain constant until all the silver chloride has combined with ammonia. On continuing to add ammonia, the pressure will again rise until it has reached the value at which the compound $2AgCl \cdot 3NH_3$ can be formed, and it will again remain constant until the lower compound has entirely disappeared. Thereafter, the pressure will increase, and will become constant when the compound AgCl . $3NH_3$ begins to be formed. *There is no gradual change of pressure* on passing from one system to another; the changes are abrupt, as is demanded by the Phase Rule (p. 72), and as experiment has conclusively proved.[1] These relation-

[1] Horstmann, *Ber.*, 1876, 9, 749. See also Jarry, *Annales Chim. Phys.*, 1899, [7], 17, 327.

ships are represented graphically in Fig. 21, which is based on the measurements of Biltz and Stollenwerk at 16·3°. On passing ammonia into a vessel containing silver chloride at 16·3°, the pressure rises until it reaches the value of 42 mm. of mercury. The compound $AgCl \cdot NH_3$ is then formed, and as there are now two solid phases present, the pressure remains constant (line A). Continued addition of ammonia leads to the complete conversion of AgCl to $AgCl \cdot NH_3$. When this has taken place, *i.e.* when the ratio $NH_3/AgCl$ in the solid equals unity, further addition of ammonia produces an increase of pressure up to 116 mm., when the compound $2AgCl \cdot 3NH_3$ begins to be formed. Again, the pressure remains constant (line B) until the compound $AgCl \cdot NH_3$ has been completely converted into $2AgCl \cdot 3NH_3$ and the ratio $NH_3/AgCl$ in the solid becomes 1·5. Thereafter, the pressure rises to 699 mm. and remains constant at this value until conversion of $2AgCl \cdot 3NH_3$ into $AgCl \cdot 3NH_3$ has taken place (line C).[1]

The reverse series of changes is observed on withdrawing ammonia from the system at 16·3°. It is important to note that the step-wise change in equilibrium pressure (dissociation pressure) at constant temperature *is indicative of the formation of more than one definite, dissociating compound.*

At temperatures above 33°, solid solutions are formed between $2AgCl \cdot 3NH_3$ and $AgCl \cdot NH_3$, and the changes of pressure, as shown in Fig. 19, are no longer so abrupt. The behaviour shown in such a case will be studied later in the case of hydrogen and palladium (p. 87).

Formation of Oxy-carbonates.—The step-wise change in equilibrium pressure (dissociation pressure) at constant temperature which is shown by the systems formed from AgCl and NH_3, and which *is indicative of the formation of more than one dissociating compound*, is shown also by certain carbonates. Thus lead carbonate, on being heated, gives rise not only to carbon dioxide and the solid phase, PbO, but also to the oxy-carbonates $3PbO \cdot 5PbCO_3$, $PbO \cdot PbCO_3$, and $2PbO \cdot PbCO_3$; and there exist, as Centnerszwer, Falk, and Awerbach [2] have shown, the following equilibria :—

		Temperature at which the dissociation pressure equals 1 atm.
A.	$8PbCO_3 \rightleftharpoons 3PbO \cdot 5PbCO_3 + 3CO_2$ . .	274°
B.	$3PbO \cdot 5PbCO_3 \rightleftharpoons 4[PbO \cdot PbCO_3] + CO_2$.	286°
C.	$3[PbO \cdot PbCO_3] \rightleftharpoons 2PbO \cdot PbCO_3 + CO_2$.	360°
D.	$2PbO \cdot PbCO_3 \rightleftharpoons 3PbO + CO_2$ . . .	412°

The relationships are shown in Fig. 22, where the dissociation temperatures are plotted against the total composition of the solid. Points *a*, *b*, and *c* on the composition axis represent the composition of the compounds $3PbO \cdot 5PbCO_3$, $PbO \cdot PbCO_3$ and $2PbO \cdot PbCO_3$

[1] For the study of other systems similar to $AgCl—NH_3$, see Biltz and Stollenwerk, *Z. anorgan. Chem.*, 1920, **114**, 174; 1921, **119**, 97; Biltz and Hüttig, *ibid.*, 1921, **119**, 115; Loyd, *J. Physical Chem.*, 1908, **12**, 398.

[2] *Z. physikal. Chem.*, 1925, **115**, 29.

respectively, and the letters A, B, C, and D refer to the systems mentioned in the above table. From the diagram it will be seen that when lead carbonate is heated in an open vessel (under atmospheric pressure), decomposition does not take place till the temperature has risen to 274°. At this temperature the pressure of the carbon dioxide becomes equal to that of the atmosphere, and continuous decomposition of the $PbCO_3$ takes place with formation of $3PbO \cdot 5PbCO_3$ and CO_2.

Since the pressure is constant (atmospheric pressure), the temperature also will remain constant so long as the two solid phases are present (system A). When all the $PbCO_3$ has undergone decomposition, the temperature must be raised to 286° before the oxy-carbonate, $3PbO \cdot 5PbCO_3$, undergoes decomposition into $PbO \cdot PbCO_3$ and CO_2. The temperature will again remain constant until complete decomposition of $3PbO \cdot 5PbCO_3$ has taken place (System B). At 360°,

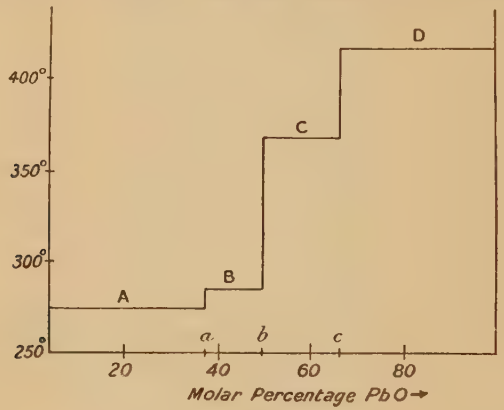


FIG. 22.

decomposition of $PbO \cdot PbCO_3$ takes place (System C), and at 412° decomposition of $2PbO \cdot PbCO_3$ (System D). At 412°, therefore, complete decomposition of lead carbonate to lead oxide and carbon dioxide can take place.

Magnesium carbonate, also, on being heated, gives rise to oxy-carbonates, and shows a behaviour similar to that found in the case of lead carbonate.[1]

Salts with Water of Crystallisation.—In the case of the dehydration of crystalline salts containing water of crystallisation, we meet with phenomena which are in all respects similar to those just studied. A salt hydrate on being heated dissociates into a lower hydrate (or anhydrous salt) and water vapour. Since we are dealing with two components—salt and water [2]—in three phases, viz. hydrate *a*,

[1] Centnerszwer and Bruzs, *Z. physikal. Chem.*, 1924, 114, 237.

[2] For the reasons for choosing anhydrous salt and water instead of salt hydrate and water as components, see p. 10.

hydrate *b* (or anhydrous salt), and vapour, the system is univariant, and to each temperature there will correspond a certain definite vapour pressure (the dissociation pressure), which will be independent of the relative or absolute amounts of the phases, *i.e.* of the amount of hydrate which has already undergone dissociation or dehydration.

The constancy of the dissociation pressure had been proved experimentally by several investigators [1] a number of years before the theoretical basis for its necessity had been given. In the case of salts capable of forming more than one hydrate, we should obtain a series of dissociation curves (*pt*-curves), as in the case of the different hydrates of copper sulphate. In Fig. 23 there are represented diagrammatically the vapour pressure curves of the following univariant systems of copper sulphate and water :—

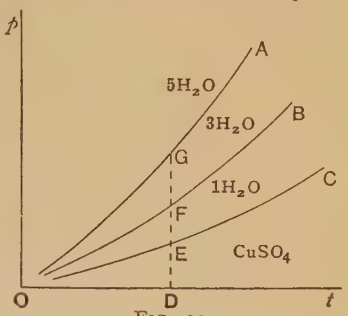


FIG. 23.

Curve OA : $CuSO_4$, $5H_2O \rightleftharpoons CuSO_4$, $3H_2O + 2H_2O$.
Curve OB : $CuSO_4$, $3H_2O \rightleftharpoons CuSO_4$, $H_2O + 2H_2O$.
Curve OC : $CuSO_4$, $H_2O \rightleftharpoons CuSO_4 + H_2O$.

Let us now follow the changes which take place on increasing the pressure of the aqueous vapour in contact with anhydrous copper sulphate, the temperature being meanwhile maintained constant. If, starting from the point D, we slowly add water vapour to the system, the pressure will gradually rise, without formation of hydrate taking place ; for at pressures below the curve OC only the anhydrous salt can exist. At E, however, the hydrate $CuSO_4,H_2O$ will be formed, and as there are now three phases present, viz. $CuSO_4$, $CuSO_4,H_2O$, and vapour, the system becomes *univariant ;* and since the temperature is constant, the pressure must also be constant. Continued addition of vapour will result merely in an increase in the amount of the hydrate, and a decrease in the amount of the anhydrous salt. When the latter has entirely disappeared, *i.e.* has passed into hydrated salt, the system again becomes *bivariant*, and passes along the line EF ; the pressure gradually increases, therefore, until at F the hydrate

[1] Many determinations of the dissociation pressure of salt hydrates, by various methods, have been carried out. See, for example, Frowein, *Z. physikal. Chem.*, 1887, **1**, 5 ; Lescoeur, *Annales Chim. Phys.*, 1890 [6], **19**, 533 ; 1890, **21**, 511 ; 1893, **28**, 237 ; 1894 [7], **2**, 78 ; 1895, **4**, 213 ; 1896, **7**, 416 ; 1896, **9**, 537 ; Tammann, *Annalen d. Physik*, 1888, **33**, 319 ; Schottky, *Z. physikal. Chem.*, 1908, **64**, 415 ; Partington, *J. Chem. Soc.*, 1911, **99**, 467 ; Partington and Huntingford, *ibid.*, 1923, **123**, 160 ; Menzies, *J. Amer. Chem. Soc.*, 1920, **42**, 1952 ; Baxter and Lansing, *ibid.*, 1920, **42**, 419 ; Wilson, *J. Amer. Chem. Soc.*, 1921, **43**, 704 ; Cumming, *J. Chem. Soc.*, 1909, **95**, 1772 ; Foote, *J. Amer. Chem. Soc.*, 1915, **37**, 288 ; Hartung, *Trans. Faraday Soc.*, 1920, **15**, Part III., 150 ; Bergmann, *J. Russ. Phys. Chem. Soc.*, 1925, **56**, 177.

$3H_2O$ is formed, and the system again becomes univariant. The three phases present are $CuSO_4,H_2O$, $CuSO_4,3H_2O$, vapour. The pressure will remain constant, therefore, until the hydrate $1H_2O$ has disappeared, when it will again increase till G is reached; here the hydrate $5H_2O$ is formed, and the pressure once more remains constant until the complete disappearance of the hydrate $3H_2O$ has taken place.

Conversely, on dehydrating $CuSO_4,5H_2O$ at constant temperature (say at 50°), we should find that the pressure would maintain the value corresponding to the dissociation pressure (47 mm.), of the system $CuSO_4,5H_2O$ — $CuSO_4,3H_2O$ — vapour, until all the hydrate $5H_2O$ had disappeared (line AB, Fig. 24);[1] further removal of water would then cause the pressure to fall *abruptly* to the pressure (30 mm.) of the system $CuSO_4,3H_2O$ — $CuSO_4,H_2O$—vapour, at which value it would again remain constant (line CD), until the trihydrate had passed into the monohydrate, when a further sudden diminution of the pressure would occur. The line of constant pressure, EF, gives the value of the vapour pressure (4·4 mm.) of the system $CuSO_4 . H_2O$—$CuSO_4$—H_2O at 50°.[2]

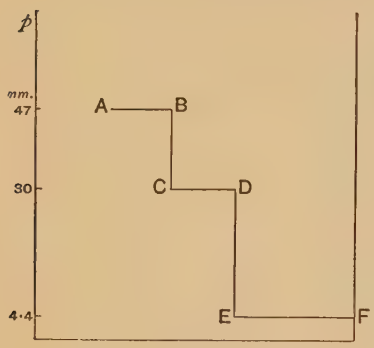


FIG. 24.

To the dissociation pressure of a salt hydrate we may apply the equation (p. 19), $\frac{d \log_e p}{dT} = \frac{Q}{RT^2}$, where Q is the heat of dissociation per gram molecule of water vapour. Since, for the vaporisation of pure water, we have the expression $\frac{d \log_e p_w}{dT} = \frac{L}{RT^2}$, where L is the latent heat of vaporisation per gram-molecule, it follows that

$$\frac{d \log_e \frac{p}{p_w}}{dT} = \frac{Q - L}{RT^2}.$$

Q — L represents the heat of combination of the salt with one gram-molecule of liquid water (heat of hydration).[3]

Efflorescence.—From Fig. 23 we are enabled to predict the conditions under which a given hydrated salt will effloresce when exposed to the air. We have just learned that copper sulphate pentahydrate,

[1] See Andreae, *Z. physikal. Chem.*, 1891, **7**, 241.

[2] The hydrates of copper sulphate have also been studied by treating copper sulphate with sulphuric acid of varying concentration (Foote, *J. Amer. Chem. Soc.*, 1915, **37**, 288).

[3] Frowein, *Z. physikal. Chem.*, 1887, **1**, 5.

for example, will not be formed unless the pressure of the aqueous vapour reaches a certain value; and that, conversely, if the vapour pressure falls below the dissociation pressure of the pentahydrate, this salt will undergo dehydration. From this, then, it is evident that a crystalline salt hydrate will effloresce when exposed to the air, if the partial pressure of the water vapour in the air is lower than the dissociation pressure of the hydrate. At the ordinary temperature the dissociation pressure of copper sulphate pentahydrate is less than the pressure of water vapour in the air, and therefore copper sulphate does not effloresce. In the case of sodium sulphate decahydrate, however, the dissociation pressure is greater than the normal vapour pressure in a room, and this salt therefore effloresces.

Indefiniteness of the Vapour Pressure of a Hydrate.—Reference has already been made (p. 78), in the case of the ammonia compounds of the metal chlorides, to the importance of the solid product of dissociation for the definition of the dissociation pressure. Similarly also in the case of a hydrated salt. A salt hydrate in contact with vapour constitutes only a bivariant system, and can exist therefore at different values of temperature and pressure of vapour, as is seen from the diagram (Fig. 23). Anhydrous copper sulphate can exist in contact with water vapour at all values of temperature and pressure lying in the field below the curve OC; and the hydrate $CuSO_4,H_2O$ can exist in contact with vapour at all values of temperature and pressure in the field BOC. Similarly, each of the other hydrates can exist in contact with vapour at different values of temperature and pressure.

From the Phase Rule, however, we learn that, in order that at a given temperature the pressure of a two-component system may be constant, there must be three phases present. Strictly, therefore, we can speak only of the vapour pressure of a *system;* and since, in the cases under discussion, the hydrates dissociate into a solid and a vapour, any statement as to the vapour pressure of a hydrate has a definite meaning *only when the second solid phase produced by the dissociation is given*. The everyday custom of speaking of the vapour pressure of a hydrated salt acquires a meaning only through the assumption, tacitly made, that the second solid phase, or the solid produced by the dehydration of the hydrate, is the *next lower* hydrate, where more hydrates than one exist. That a hydrate always dissociates in such a way that the next lower hydrate is formed is, however, by no means certain; indeed, cases have been met with where apparently the anhydrous salt, and not the lower hydrate (the existence of which was possible), was produced by the dissociation of the higher hydrate.[1]

That a salt hydrate can exhibit different vapour pressures according to the solid product of dissociation, can not only be deduced theoretically, but it has also been shown experimentally to be a fact. Thus $CaCl_2,6H_2O$ can dissociate into water vapour and either of two lower

[1] Ostwald, *Lehrbuch*, II., **2**, 538.

hydrates, each containing four molecules of water of crystallisation, and designated respectively as $CaCl_2,4H_2O\alpha$ and $CaCl_2,4H_2O\beta$. Roozeboom [1] has shown that the vapour pressure which is obtained differs according to which of these two hydrates is formed, as can be seen from the following figures :—

Temperature.	Pressure of system.	
	$CaCl_2, 6H_2O$; $CaCl_2, 4H_2O\alpha$; vapour.	$CaCl_2, 6H_2O$; $CaCl_2, 4H_2O\beta$; vapour.
− 15°	0·027 cm.	0·022 cm.
0°	0·092 ,,	0·076 ,,
+ 10°	0·192 ,,	0·162 ,,
20°	0·378 ,,	0·315 ,,
25°	0·508 ,,	0·432 ,,
29·2°	—	0·567 ,,
29·8°	0·680 ,,	—

By reason of the non-recognition of the importance of the solid dissociation product for the definition of the dissociation pressure of a salt hydrate, many of the older determinations lose much of their value.

Suspended Transformation.—Just as in systems of one component we found that a new phase was not necessarily formed when the conditions for its existence were established, so also we find that even when the vapour pressure is lowered below the dissociation pressure of a system, dissociation does not necessarily occur. This is well known in the case of Glauber's salt, first observed by Faraday. Undamaged crystals of $Na_2SO_4,10H_2O$ could be kept unchanged in the open air, although the vapour pressure of the system $Na_2SO_4,10H_2O$—Na_2SO_4—vapour is greater than the ordinary pressure of aqueous vapour in the air. That is to say, the possibility of the formation of the new phase Na_2SO_4 was given ; nevertheless, this new phase did not appear, and the system therefore became metastable, or unstable with respect to the anhydrous salt. When, however, a trace of the new phase—the anhydrous salt—was brought in contact with the hydrate, transformation occurred ; the hydrate effloresced.

The possibility of suspended transformation or the non-formation of the new phases must also be granted in the case where the vapour pressure is raised above that corresponding to the system hydrate—anhydrous salt (or lower hydrate)—vapour ; in this case the formation of the higher hydrate becomes a possibility, but not a certainty. Although there is no example of this known in the case of hydrated salts, the suspension of the transformation has been observed in the case of the compounds of ammonia with the metal chlorides (p. 76). Horstmann,[2] for example, found that the pressure of ammonia in

[1] *Z. physikal. Chem.*, 1889, 4, 43. [2] *Ber.*, 1876, 9, 749.

contact with $2AgCl,3NH_3$ could be raised to a value higher than the dissociation pressure of $AgCl,3NH_3$ without this compound being formed. We see, therefore, that even when the existence of the higher compound in contact with the lower became possible, the higher compound was not immediately formed.

Range of Existence of Hydrates.—In Fig. 23 the vapour pressure curves of the different hydrates of copper sulphate are represented as maintaining their relative positions throughout the whole range of temperatures. But this is not necessarily the case. It is possible that at some temperature the vapour pressure curve of a lower hydrate may cut that of a higher hydrate. At temperatures above the point of intersection, the lower hydrate would have a higher vapour pressure than the higher hydrate, and would therefore be metastable with respect to the latter. The range of stable existence of the lower hydrate would therefore end at the point of intersection. This appears to be the case with the two hydrates of sodium sulphate, to which reference will be made later.

Constancy of Vapour Pressure and the Formation of Compounds.—We have seen in the case of the systems discussed in this section that the continued addition of the vapour phase to the system, at constant temperature, causes an increase in the pressure until at a definite value of the pressure a dissociating compound is formed; the pressure then becomes constant, and remains so, until one of the solid phases has disappeared. Conversely, on withdrawing the vapour phase, the pressure remains constant so long as any of the dissociating compound is present, independently of the degree of the decomposition (p. 81). In other words, when compounds are formed which dissociate with formation of a solid and of a gaseous phase, there is a step-wise change in the equilibrium pressure when the gas phase is added to or withdrawn from the system at constant temperature. This behaviour has been employed for the purpose of determining whether or not definite chemical compounds are formed. By this method, Ramsay [1] found that lead monoxide can form the two hydrates $2PbO . H_2O$ and $3PbO . H_2O$; and by this method also the existence of the oxy-carbonates of lead and of magnesium was established.

II. (*b*) The Gas is Absorbed by the Solid Component and No Compound is Formed.

It has already been pointed out that when the gas is absorbed by the solid component without formation of a compound, the system is bivariant. There will therefore be no "breaks" in the pressure-composition curve. Continued addition of the vapour phase will lead to a continuous change in the composition of the solid phase (a solid solution), and to a continuous increase of the pressure. Similarly, withdrawal of the gaseous product of dissociation will lead to a continuous change in the composition of the solid phase and diminution

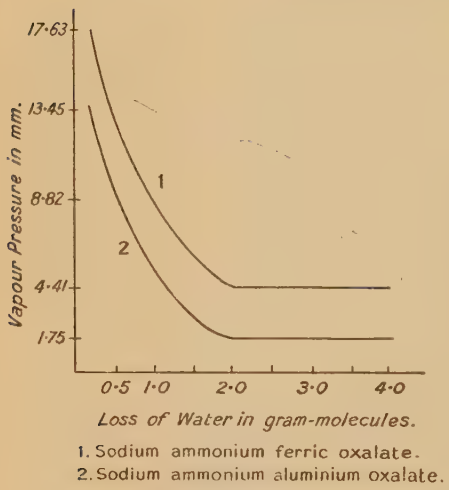
[1] *J. Chem. Soc.*, 1877, **32**, 395.

of the gas or vapour pressure. Thus, Tammann [1] found that when the hydrated silicates, known as zeolites, are dehydrated at constant temperature, there is a continuous diminution of the vapour pressure. Similarly, the dehydration curve of the so-called white tungstic acid is continuous and gives no indication of the existence of the compound $WO_3 . 2H_2O$.[2] Continuous dehydration curves are obtained also in the case of the hydrates of silicic acid, and of the oxalates of thorium, zirconium, lanthanum, yttrium, and cerium.[3]

II. (*c*) The Gas is Absorbed by the Solid Component and a Compound is also Formed.

When sodium ammonium ferric oxalate, $Na_3(NH_4)_3Fe_2(C_2O_4)_6, 7H_2O$, and sodium ammonium aluminium oxalate,

$$Na_3(NH_4)_3Al_2(C_2O_4)_6,7H_2O,$$



1. Sodium ammonium ferric oxalate.
2. Sodium ammonium aluminium oxalate.

Fig. 25.

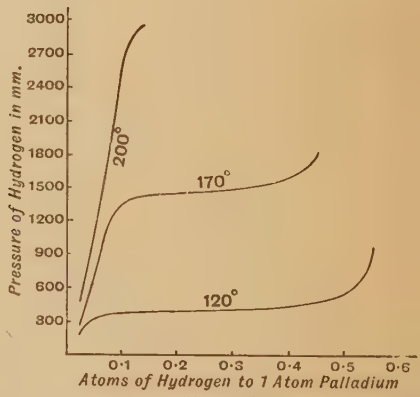


Fig. 26.

are dehydrated at 25°, the vapour pressure diminishes continuously with loss of water from the hydrated salts until two gram molecules of water have been lost. The vapour pressure then remains constant until the pentahydrate has been converted into the monohydrate (Fig. 25).[4]

[1] *Z. physikal. Chem.*, 1898, **27**, 323.
[2] Hüttig, *Z. anorgan. Chem.*, 1923, **122**, 44.
[3] Löwenstein, *ibid.*, 1909, **63**, 69.
[4] *Ibid.*, 1909, **63**, 69.

II. (*d*) Absorption of Gas and Formation of Two Partially Miscible Solid Solutions.

Palladium and Hydrogen.—The phenomenon of the absorption of hydrogen by palladium, to which Graham gave the name "occlusion," is one that has claimed the attention of several investigators. Although Graham was not of opinion that a compound is formed, but rather that the gas undergoes very great condensation, acts as a quasi-metal (to which he gave the name hydrogenium), and forms a homogeneous alloy with the palladium, later investigations, especially those of Troost and Hautefeuille,[1] pointed to the formation of a definite chemical compound, having the formula Pd_2H. This conclusion has, however, not been confirmed by subsequent investigation.[2]

Roozeboom and Hoitsema [3] sought to arrive at a final decision as to the nature of the phenomenon by an investigation of the equilibrium between hydrogen and palladium on the basis of the Phase Rule classification given on page 72. If a compound is formed, diminution of volume would cause no increase of pressure, but only an increase in the amount of the compound.

As this is the only case of gas absorption which has been accurately studied from this point of view, a brief account of the results obtained will be given here, although these are not so clear and free from ambiguity as one would desire.

The scientists just mentioned investigated the variation of the pressure of hydrogen with the amount absorbed by the metal at different temperatures, and a few of their results, typical of all, are represented graphically in Fig. 26; the curves indicating the variation of the gas pressure with the concentration of the hydrogen in the palladium at the temperatures 120°, 170°, and 200°. As can be seen, the curve consists of three parts, an ascending portion which passes gradually and continuously into an almost horizontal but slightly ascending middle part, which in turn passes without break into a second rapidly ascending curve. This, as Fig. 26 indicates, is the general form of the curve; but the length of the middle portion varies with the temperature, being shorter at higher than at lower temperatures.

What is the interpretation to be put on these curves? With regard to the two end portions, these represent bivariant, two-phase systems, consisting of a solid solution and gas. They correspond, therefore, to curve AB in Fig. 20 (p. 73). If the middle portion were horizontal, it would indicate either the formation of a compound or of two immiscible solid solutions. If a compound Pd_2H were formed, then the middle portion would at all temperatures end at the same value of the concentration, viz. that corresponding to 0·5 atom of hydrogen to

[1] *Annales Chim. Phys.*, 1874 [5], **2**, 279.
[2] Hoitsema, *Z. physikal. Chem.*, 1895, **17**, 1; Dewar, *Phil. Mag.*, 1874 [4], **47**, 324, 342; Mond, Ramsay and Shields, *Proc. Roy. Soc.*, 1897, **62**, 290.
[3] *Loc. cit.*

1 atom of palladium. As the figure shows, however, this is not the case; the higher the temperature, the lower is the concentration at which the middle passes into the terminal portion of the curve. Such a behaviour would, however, agree with the assumption of the formation of two solid solutions, the " miscibility " of which increases with the temperature, as in the case of the liquid solutions of phenol and water (p. 91). Nevertheless, although the assumption of the formation of two solid solutions is more satisfactory than that of the formation of a compound, it does not entirely explain the facts. If two solid solutions are formed, the pressure curve should be horizontal, but this is not the case; and the deviation from the horizontal does not appear to be due to impurities either in the gas or in the metal, but is apparently a peculiarity of the system. Further, the gradual instead of abrupt passage of the three portions of the curve into one another remains unexplained. Hoitsema has expressed the opinion that the occlusion of hydrogen by palladium is a process of continuous absorption, the peculiar form of the curve—the flat middle portion—being possibly due to a condensation of the gas, even at temperatures far above the critical temperature of liquid hydrogen.

In more recent years the occlusion of hydrogen by palladium has been the subject of further study.[1] From these investigations it becomes clear that various factors play a part in connection with the occlusion of hydrogen by palladium. More especially does it appear that surface adsorption is a factor which introduces a complication into the system. Besides the surface adsorption, however, diffusion of the hydrogen into the palladium occurs, whether accompanied by the formation of a definite compound or not, cannot yet be definitely stated; and it appears to be doubtful whether under ordinary circumstances, the distribution of the hydrogen throughout the palladium is uniform. The interpretation of the behaviour of palladium towards hydrogen, therefore, is complicated and rendered somewhat obscure by the occurrence of other factors than those merely of solution or of compound formation, and a final, satisfactory interpretation cannot yet be given.

X-ray analysis of the palladium—hydrogen systems gives results which are in harmony with the view that hydrogen and palladium form two crystalline solid phases, one of which is practically pure palladium and the other a saturated solution of hydrogen in palladium.[2]

[1] Paal and Amberger, *Ber.*, 1905, **38**, 1394, 1398, 1406; Paal and Gerum, *ibid.*, 1908, **41**, 805, 818; Sieverts, *Z. physikal. Chem.*, 1910, **74**, 277; *Ber.*, 1910, **43**, 897; *Internat. Zeitschr. für Metallographie*, 1912, **3**, 51, Tabelle 12; Holt, Edgar, and Firth, *Z. physikal. Chem.*, 1913, **82**, 513; Andrew and Holt, *Proc. Roy. Soc.*, 1913, A., **89**, 170; Holt, *ibid.*, 1914, A., **90**, 226; Wolf, *Z. physikal. Chem.*, 1914, **87**, 575; Sieverts, *ibid.*, 1914, **88**, 103, 451: Firth, *J. Chem. Soc.*, 1920, **117**, 171; 1921, **119**, 1120; General Discussion, *Trans. Faraday Soc.*, 1919, **14**, 232; Oxley, *Proc. Roy. Soc.*, 1922, **101**, A., 264.

[2] Yamada, *Phil. Mag.*, 1923, **45**, 241; McKeehan, *Phys. Rev.*, 1923, **21**, 334.

CHAPTER VII.

SYSTEMS OF TWO COMPONENTS (*Continued*).

B. Systems Formed of Two Liquid Phases only. Solutions of Liquids in Liquids.

When mercury and water are brought together, the two liquids remain side by side without mixing. Strictly speaking, mercury undoubtedly dissolves to a certain extent in the water, and water no doubt dissolves, although to a less extent, in the mercury; the amount of substance passing into solution is, however, so minute, that it may, for all practical purposes, be left out of account, so long as the temperature does not rise much above the ordinary.[1] On the other hand, if alcohol and water be brought together, complete miscibility takes place, and one homogeneous solution is obtained. Whether water be added in increasing quantities to pure alcohol, or pure alcohol be added in increasing amount to water, at no point, at no degree of concentration, is a system obtained containing more than one liquid phase. At the ordinary temperature, water and alcohol can form only two phases, liquid and vapour. If, however, water be added to ether, or if ether be added to water, solution will not occur to an indefinite extent; but a point will be reached when the water or the ether will no longer dissolve more of the other component, and a further addition of water on the one hand, or ether on the other, will cause the formation of two liquid layers, one containing excess of water, the other excess of ether. We shall, therefore, expect to find all grades of miscibility, from almost perfect immiscibility to perfect miscibility, or miscibility in all proportions. In cases of complete immiscibility, the components do not affect one another, and the system therefore remains unchanged. Such cases do not call for treatment here. We have to concern ourselves here only with the second and third cases, viz. with cases of complete and of partial miscibility. There is no essential difference between the two classes, for, as we shall see, the one passes into the other with change of temperature. The formal separation

[1] That mercury does dissolve in water can be argued from analogy, say, with mercury and bromonaphthalene. At the ordinary temperature these two liquids appear to be quite insoluble the one in the other, but at a temperature of 280° the mercury dissolves in appreciable quantity; for on heating a tube containing bromonaphthalene over mercury the latter sublimes *through* the liquid bromonaphthalene and condenses on the upper surface of the tube.

into two groups is based on the miscibility relations at ordinary temperatures.

Partial or Limited Miscibility.—In accordance with the Phase Rule, a pure liquid in contact with its vapour constitutes a univariant system. If, however, a small quantity of a second substance is added, which is capable of dissolving in the first, a bivariant system will be obtained; for there are now two components and, as before, only two phases—the homogeneous liquid solution and the vapour. At constant temperature, therefore, both the composition of the solution and the pressure of the vapour can undergo change; or, if the composition of the solution remains unchanged, the pressure and the temperature can alter. If the second (liquid) component is added in increasing amount, the liquid will at first remain homogeneous, and its composition and pressure will undergo a continuous change; when, however, the concentration has reached a definite value, solution no longer takes place, and two liquid phases are produced. Since there are now three phases present, two liquid phases and vapour, the system is univariant; at a given temperature, therefore, the concentration of the components in the two liquid phases, as well as the vapour pressure, must have definite values. Addition of one of the components, therefore, cannot alter the concentrations or the pressure, but can only cause a change in the relative amounts of the phases.

The two liquid phases can be regarded, the one as a solution of the component I. in component II., the other as a solution of component II. in component I. If the vapour phase be removed and the pressure on the two liquid phases be maintained constant (say, at atmospheric pressure), the system will still be univariant, and to each temperature there will correspond a definite concentration of the components in the two liquid phases; and addition of excess of one will merely alter the relative amounts of the two solutions. As the temperature changes, the composition of the two solutions will change, and there will therefore be obtained two solubility curves, one showing the solubility of component I. in component II., the other showing the solubility of component II. in component I. Since heat may be either evolved or absorbed when one liquid dissolves in another, the solubility may diminish or increase with rise of temperature (theorem of Le Chatelier, p. 18). The two solutions which at a given temperature coexist in equilibrium are known as *conjugate solutions*.

The solubility relations of partially miscible liquids have been studied by Guthrie,[1] Alexejeff,[2] Rothmund,[3] Timmermans,[4] Flaschner[5] and others. A considerable variety of curves have been obtained, and we shall therefore discuss only a few of the different cases which may be taken as typical of the rest.

[1] *Phil. Mag.*, 1884 [5], **18**, 22, 495. [2] *Annalen d. Physik*, 1886, **28**, 305.
[3] *Z. physikal. Chem.*, 1898, **26**, 433.
[4] *Bull. Soc. chim. Belg.*, 1906, **20**, 386; *Proc. K. Akad. Wetensch. Amsterdam*, 1910, **13**, 507; *Z. physikal. Chem.*, 1907, **58**, 144.
[5] *J. Chem. Soc.*, 1908, **93**, 1000; 1909, **95**, 668.

Phenol and Water.—When phenol is added to water at the ordinary temperature, solution takes place, and a homogeneous liquid is produced. When, however, the concentration of the phenol in the solution has risen to about 8 per cent., phenol ceases to be dissolved; and a further addition of it causes the formation of a second liquid phase, which consists of excess of phenol and a small quantity of water. In ordinary language it may be called a solution of water in phenol. If now the temperature is raised, this second liquid phase will disappear, and a further amount of phenol must be added in order to produce a separation of the liquid into two layers. In this way, by increasing the amount of phenol and noting the temperature at which the two layers disappear, the so-called solubility curve of phenol in water can be obtained.[1] The solubility increases with rise of temperature.

In a similar manner the solubility of water in liquid phenol can be

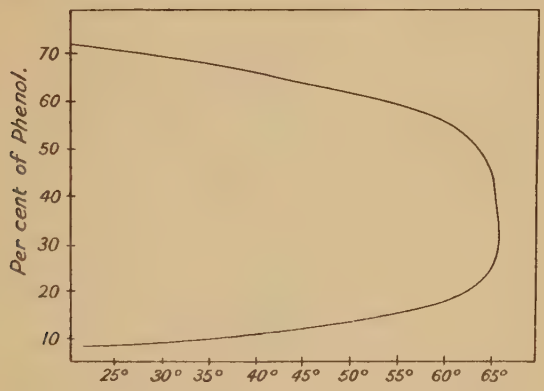


FIG. 27.

determined, and in this case also, it is found, the solubility increases with rise of temperature.

Since, with rise of temperature, the concentration of water in the phenol layer, and, similarly, the concentration of phenol in the aqueous layer increase, the composition of the two solutions must become more and more nearly the same, and at a certain temperature the two solutions become identical. At this point, the two liquid solutions pass into one homogeneous solution. The temperature, however, at which two phases become identical is known as a critical temperature, and, accordingly, the temperature at which two conjugate solutions become

[1] See Findlay, *Practical Physical Chemistry* (Longmans). On cooling the homogeneous solution, a turbidity generally makes its appearance quite sharply at the temperature at which the line representing the composition of the solution cuts the solubility curve. Supersaturation may, however, take place, and has been observed in the case of nitrobenzene and water and carbon disulphide and water (Davis, *J. Amer. Chem. Soc.*, 1916, **38**, 1166). See also Flaschner, *Z. physikal. Chem.*, 1908, **62**, 493; Gürtler, *Z. anorgan. Chem.*, 1904, **40**, 225.

identical is known as the *critical solution temperature.*[1] The composition of the solution at this point may be called the *critical composition.* One may also speak of the consolute concentration of the solution.

The mutual solubility of phenol and water has been determined by a number of investigators.[2] The values obtained by Hill and Malisoff are given in the following table and represented graphically in Fig. 27 :—

PHENOL AND WATER.

C_1 and C_2 are the percentage amounts of phenol by weight in the two layers.

Temperature.	C_1.	C_2.
20°	72·16	8·36
25°	71·28	8·66
30°	69·90	9·22
35°	67·63	9·91
54·83°	59·22	—
57·30°	—	14·87
62·55°	51·87	—
62·74°	—	19·35
65·24°	44·09	—
65·79°	—	30·21
65·84°	34·23	32·23

On plotting these results, as shown in Fig. 26, the critical solution temperature is found to be 65·85° ± 0·15°, and the critical concentration, 34·0 per cent. of phenol. At any temperature below the critical solution temperature, two conjugate solutions containing water and phenol in different concentration can exist together ; at all temperatures above the critical solution temperature, only homogeneous solutions of phenol and water can be obtained. Above the critical solution temperature, phenol and water are miscible in all proportions.

The lower limits of the solubility curves will lie at the freezing-points of the solutions.

From Fig. 26 it is easy to predict the effect of bringing together water and phenol in any given quantities at any temperature. When phenol and water are brought together in amounts and at any temperature represented by a point in the area enclosed by the solubility curve, separation into two liquid layers will take place, whereas, when the total composition of the mixture and the temperature are represented by a point lying outside the solubility curve, only one homogeneous solution will be formed.

[1] Orme Masson, *Z. physikal. Chem.*, 1891, **7**, 500.

[2] See especially Rothmund, *Z. physikal. Chem.*, 1898, **26**, 443 ; Timmermans, *Z. physikal. Chem.*, 1907, **58**, 184 ; *J. Chim. Phys.*, 1923, **20**, 491 ; Hill and Malisoff, *J. Amer. Chem. Soc.*, 1926, **48**, 918.

Methylethylketone and Water.—In the case just described, the solubility of each component in the other increases continuously with the temperature. There are, however, cases where a maximum or minimum of solubility is found, *e.g.* methylethylketone and water. The curve which represents the equilibria between these two substances is given in Fig. 28, the concentration values being contained in the following table :—[1]

METHYLETHYLKETONE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
− 20°	40·1	89·4
0°	30·6	89·6
+ 20°	22·6	90·1
40°	18·6	89·6
60°	16·5	88·2
80°	15·7	85·8
100°	16·4	82·6
120°	18·6	77·3
140°	26·4	65·5
150°	45·0	45·0

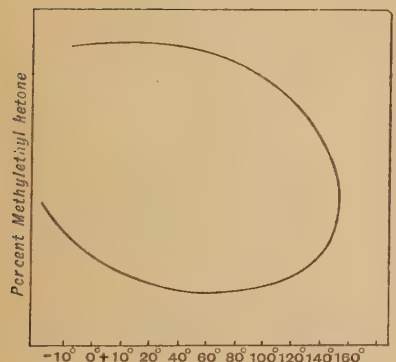


FIG. 28.

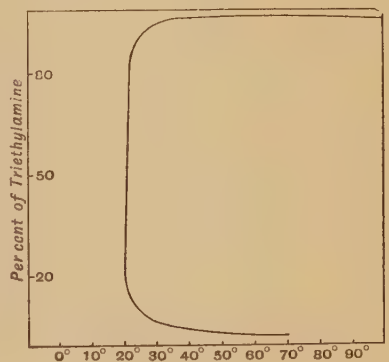


FIG. 29.

These numbers and Fig. 28 show clearly the occurrence of a minimum in the solubility of the ketone in water, and also a minimum (at about 10°) in the solubility of water in methylethylketone. Minima of solubility have also been found in other cases.

Triethylamine and Water.—Although in most of the cases studied the solubility of one liquid in another increases with rise of temperature, this is not so in all cases. Thus, at temperatures below 18°, triethylamine and water mix together in all proportions; but, on raising the temperature, the homogeneous solution becomes turbid

[1] Rothmund, *Z. physikal. Chem.*, 1898, **26**, 433.

and separates into two layers. In this case, therefore, the critical solution temperature is found in the direction of lower temperature, not in the direction of higher.[1] This behaviour is clearly shown by the graphic representation in Fig. 29, and also by the numbers in the following table :—

TRIETHYLAMINE AND WATER.

Temperature.	C_1 per cent.	C_2 per cent.
70°	1·6	—
50°	2·9	—
30°	5·6	96
25°	7·3	95·5
20°	15·5	73
± 18·5°	± 30	± 30

General Form of the Concentration-Temperature Curve.— From the preceding discussion it will be clear that the solubility curve of two partially miscible liquids may show either an upper or a lower critical solution temperature. In the case of phenol and water and of methylethyl ketone and water, the open ends of the solubility curve end at the freezing-points of the solutions. In the case of liquids having a lower critical solution temperature, the question arises : What will happen when the solubility determinations are extended to higher and higher temperatures ? Since for all liquids there is a point (critical point) at which the liquid and gaseous states become identical, and since all gases are miscible in all proportions, it has been argued that there must be some upper temperature at which liquids will become completely miscible. It may, however, happen that the critical point of one of the liquids is reached before the critical solution temperature, and the solubility curve will, therefore, remain open.[2] One is nevertheless led to conclude from the behaviour of many systems, that the general form of the concentration-temperature curve is that of a closed ring, having both an upper and a lower critical solution temperature, and a number of such curves have, indeed, been obtained. Thus, nicotine and water are completely miscible at temperatures below 60° and above 210° (Fig. 30),[3] and closed solubility curves are also given by the liquids, water—β-picoline, water—methyl piperidine, glycerol—guaiacol, glycerol—benzylethylamine, etc.[4]

[1] A similar behaviour is found in the case of diethylamine and water (R. T. Lattey, *Phil. Mag.*, 1905 [6], **10**, 397). See also Rothmund, *Z. physikal. Chem.*, 1898, **26**, 433 ; Flaschner, *ibid.*, 1908, **62**, 493.

[2] See also Dolgolenko, *Z. physikal. Chem.*, 1908, **62**, 499.

[3] Hudson, *Z. physikal. Chem.*, 1904, **47**, 113.

[4] Flaschner, *J. Chem. Soc.*, 1909, **95**, 668 ; Flaschner and McEwen, *ibid.*, 1908, **93**, 1000 ; McEwen, *ibid.*, 1923, **123**, 2284 ; Parvatiker and McEwen, *ibid.*, 1924, **125**, 1484.

The view that the general form of the concentration-temperature curve is that of a closed ring is supported by the fact that pairs of liquids which, under atmospheric pressure, give curves exhibiting only a lower or an upper critical solution temperature, give closed-ring solubility curves when the pressure is increased (p. 96). Thus, under a pressure of 150 atmospheres, methylethylketone and water give a closed-ring solubility curve with critical solution temperatures at — 6° and 133°.[1]

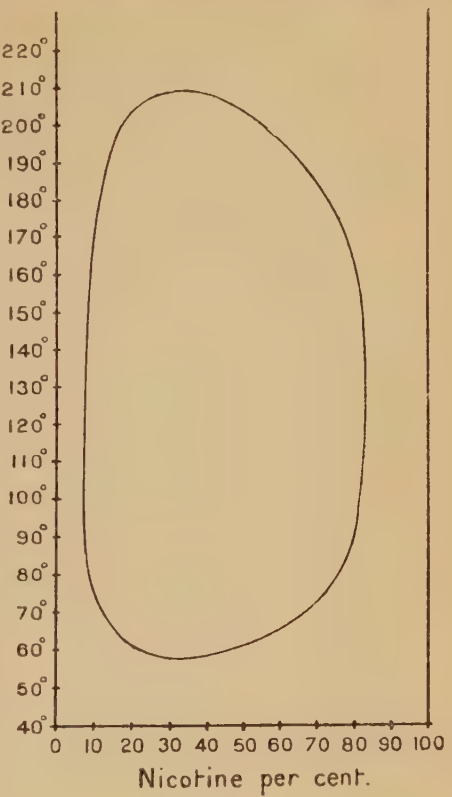


FIG. 30.

With regard to the closed end of the curve, it may be said that it is continuous. The critical solution point is not the intersection of two curves, for such a break in the continuity of the curve could occur only if there were some discontinuity in one of the phases. No such discontinuity exists. The curve is, therefore, not to be considered as two solubility curves cutting at a point, but a curve of equilibrium between two phases which are undergoing continuous change.[2]

Influence of Pressure on the Critical Solution Temperature.—At the critical solution point the system exists in only two phases—liquid and vapour. It ought, therefore, to possess two degrees of freedom. The restriction is, however, imposed that the composition of the two liquid phases, coexisting at a point infinitely near to the critical point, becomes the same; and this disposes of one of the degrees of freedom. The system is therefore univariant; and at a given temperature the pressure will have a definite value. Conversely, if the pressure is fixed (as is the case when the system is under the pressure of its own vapour), then the temperature will also be fixed; that

[1] Kohnstamm and Timmermans, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1021.

[2] For a discussion of the equilibria in the case of partially miscible liquids, see Büchner, *Z. physikal. Chem.*, 1906, **56**, 257.

is, the critical solution temperature has a definite value depending only on the substances. If the vapour phase is omitted, the temperature of the critical solution point will alter with the pressure.

The change of the critical solution temperature with the pressure depends, according to the theorem of Le Chatelier and the equation of Clapeyron, on the change of volume which occurs when one of the components in the fused state is added to the nearly saturated solution.[1] It has been made the subject of experimental investigation by Kohnstamm and Timmermans,[2] and some of the results obtained are given in the following tables :—

Water and *Sec.*-butyl Alcohol.

Pressure in kgm. per sq. cm.	Lower critical solution temperature.	$\frac{dt}{dp}$ per kgm.	Upper Critical solution temperature.	$\frac{dt}{dp}$ per kgm.
1	—[3]	—	113·8°	− 0·071
100	5·3°	> + 0·1375	—	—
120	—	—	105·3°	− 0·041
200	17·8°	+ 0·123	—	—
300	24·8°	+ 0·070	—	—
500	36·7°	+ 0·059	—	—
600	42·7°	+ 0·060	85·8°	− 0·045
700	49·6°	+ 0·069	81·3°	− 0·078
800	58·6°	+ 0·090	73·5°	—
830	65°	—	65°	—

From the above table it is clear that the lower critical solution temperature is raised, and the upper critical solution temperature is lowered, by increase of pressure. Under a pressure of 830 kgm. per sq. cm. the two critical solution points coincide. Under pressures higher than this, complete miscibility exists at all temperatures. A similar behaviour is found in the case of water and methylethylketone.

Whereas a lower critical solution temperature is always raised by increase of pressure, an upper critical solution temperature may be either raised or lowered. In the case of water and *sec.*-butyl alcohol, water and methylethylketone, water and isobutyric acid, the upper critical solution temperature is lowered by increase of pressure; in the case of water and phenol it is raised, as the following numbers show :—

[1] See Timmermans, *Bull. Soc. Chim. Belg.*, 1909, **23**, 433; *Acad. R. Belg., Classe des Sci.*, 1919, p. 753.

[2] Kohnstamm and Timmermans, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **15**, 1021; Timmermans, *Arch. Néerland.*, 1922 [3], **6**, 127.

[3] Under atmospheric pressure, water and *sec.*-butyl alcohol are only partially miscible at all temperatures down to the freezing-point of the solution, namely, − 8·45°. A lower critical solution temperature makes its appearance only when the pressure is increased.

WATER AND PHENOL.

Pressure in kgm. per sq. cm.	Critical solution temperature.	$\frac{dt}{dp}$
10	66·23°	
		+ 0·0029
200	66·78°	
		+ 0·0040
600	68·39°	
		+ 0·0055
1000	70·61°	

Similarly, increase of pressure raises the critical solution temperature of cyclohexane and methyl alcohol.

Influence of Foreign Substances on the Critical Solution Temperature.—For a given pressure, the critical solution temperature is, as we have seen, a perfectly defined point. It is, however, altered to a very marked extent by the addition of a foreign substance (impurity), which dissolves either in one or in both of the partially miscible liquids. Although these systems are really three-component systems, and will be discussed more fully at a later point, the effect of small additions of a substance to a system of two liquid components is of such practical importance, that a brief discussion of the regularities observed may be given here.[1]

When the third substance *dissolves in only one of the two liquids*, the mutual solubility of the latter is diminished, and the temperature at which the system becomes homogeneous is raised, in the case of liquids having an upper critical solution temperature, and lowered in the case of liquids having a lower critical solution temperature. The elevation (or the lowering) of temperature depends not only on the nature and amount of the added substance, but also on the composition of the liquid mixture. When the two liquids are present in the proportions of the critical composition, it is found that, for concentrations of the addendum (non-electrolyte) less than about 0·1 molar, the elevation (or depression) of the critical solution temperature is nearly proportional to the amount added. The elevation (or depression) of the critical solution temperature for small equi-molecular quantities of different substances is, however, not constant, but depends on the nature of the substance added.[2] In the following tables are given the values for the elevation of the critical solution temperature of phenol and water by naphthalene (soluble only in phenol) and by potassium chloride (soluble only in water). E represents the " molecular elevation " of the critical solution temperature :—

[1] See Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129; Schükareff, *ibid.*, 1910, **71**, 90.

[2] Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129; Drucker, *Rec. trav. chim.*, 1923, **42**, 552; Boutari and Nabot, *Compt. rend.*, 1923, **176**, 1618; Bailey, *J. Chem. Soc.*, 1923, **123**, 2579.

Water—Phenol—Naphthalene.				Water—Phenol—Potassium Chloride.			
Concentration of naphthalene.		Critical solution temperature.	E.	Concentration of potassium chloride.		Critical solution temperature.	E.
Molar.	Per cent.			Molar.	Per cent.		
—	—	65·3°	—	—	—	65·3°	—
0·0148	0·190	68·5°	216·2°	0·146	1·09	77·4°	83°
0·0343	0·440	72·6°	212·8°	0·292	2·18	87·3°	75°
0·059	0·76	77·6°	207·7°	0·410	3·06	94·0°	70°
0·081	1·04	82·0°	206·4°				
0·124	1·59	89·6°	196·1°				

According to Duckett and Patterson,[1] the elevation of the critical solution temperature of phenol and water by salts is the sum of two values, depending on the ions; and the anions and kations may be arranged, according to their influence, in a series which is almost identical with the Hofmeister series (for the coagulation of egg albumin).

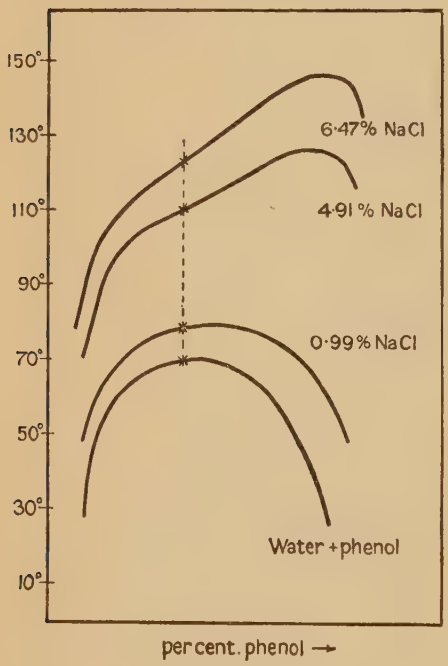


Fig. 31.

Owing to the fact that the influence of the added substance on the saturation temperature of two liquids depends on the composition of the mixture, the solubility curve becomes distorted, and the maximum temperature of saturation is no longer shown by the system in which the two liquids are present in amounts corresponding with the critical composition (Fig. 31). This point will be further discussed in connection with three-component systems.

When the third substance *dissolves in both the liquids*, the effect on

[1] *J. Physical Chem.*, 1925, **29**, 294. See also Patterson and Duckett, *J. Chem. Soc.*, 1925, **127**, 624; Carrington, Hickson and Patterson, *ibid.*, 1925, **127**, 2544; Howard and Patterson, *ibid.*, 1926, pp. 2787, 2791.

the critical solution temperature will depend on the relative solubility of the added substance in the two liquids. If the solubility in the two liquids is very different, an upper critical solution temperature may still be raised, and a lower critical solution temperature may be depressed, although to a much less extent than when the added substance is soluble in only one of the liquids. When, however, the solubility of the addendum in the two liquids is of the same order, the mutual solubility of the liquids will be increased. Consequently, an upper critical solution temperature will be lowered, and a lower critical solution temperature will be raised, as is shown by the numbers in the following tables :—

WATER—PHENOL—SUCCINIC ACID.

Concentration of succinic acid.		Critical solution temperature.	E.
Moles.	Per cent.		
0·190	2·25	51·6	− 72°
0·321	3·81	40·3°	− 78°
0·685	8·09	− 8·0°	− 105°

WATER—PHENOL—SODIUM OLEATE.

Concentration of sodium oleate.		Critical solution temperature.	E.
Moles.	Per cent.		
0·0324	0·98	43·7°	− 673°
0·0575	1·75	25·8°	− 687°
0·083	2·51	9·2°	− 679°

WATER—*Sec.*-BUTYL ALCOHOL—HYDROQUINONE.

Concentration of hydroquinone.		Upper critical solution temperature.	Lower critical solution temperature.
Moles.	Per cent.		
0	0	113·5°	Below cryohydric point
0·639	7·03	71·0°	16·5°
0·747	8·21	62·2°	25·0°

The very large effect produced by sodium oleate has been applied industrially to the production, at the ordinary temperature, of a highly concentrated solution of tar-acids (phenol and cresols), used as a disinfectant under the name of lysol.

The great sensitiveness of the critical solution temperature to impurities is of great importance and has found very valuable application not only in analytical practice for distinguishing between related substances, such as different oils and fats, but also in the laboratory

as a delicate test for the purity of a liquid.[1] The property has been also applied to the medical examination of urine.[2]

Presence of Vapour Phase.—In the preceding discussion the presence of the vapour phase has been definitely excluded. Since, however, the influence of pressure on the mutual solubility of liquids is, as we have seen, comparatively small, the value of the solubility under the pressure of the vapour of the liquids will not greatly differ from the value under atmospheric pressure. While it is beyond the scope of this book to discuss in any detail the behaviour of two-component systems in which liquid and vapour phases coexist, a few brief remarks may nevertheless be made.

When the liquids are miscible in all proportions, or where only one liquid and one vapour phase are present, the system is bivariant; and two of the variables, pressure, temperature or concentration of the components, must be arbitrarily chosen before the system becomes defined. For this reason the Phase Rule affords only a slight guidance in the study of such equilibria. All that the Phase Rule can tell us in connection with these solutions, is that at constant temperature the vapour pressure of the solution varies with the composition of the liquid phase; and if the composition of the liquid phase remains unchanged, the pressure also must remain unchanged. This constancy of composition is exhibited not only by pure liquids, but also by liquid solutions in all cases where the vapour pressure of the solution reaches a maximum or minimum value. This is the case, for example, with mixtures of constant boiling-point.[3]

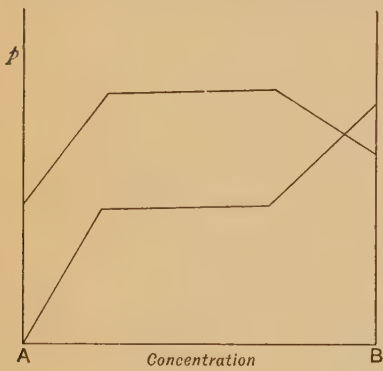


FIG. 32.

If, however, two liquid phases are formed, the system becomes univariant: and if one of the variables, say the temperature, is arbitrarily fixed, the system no longer possesses any degree of freedom, *When two liquid phases are formed, therefore, the concentrations and the total vapour pressure of the system have definite values, which are main-*

[1] Crismer, *Bull. de l'Association des Chimistes*, 1895, **9**, 145; 1896, **10** 312; 1904, **18**, 1; 1906, **20**, 294; *Z. physikal. Chem.*, 1895, **20**, 390; Flaschner, *J. Chem. Soc.*, 1909, **95**, 677; Dolgolenko, *Z. physikal. Chem.*, 1908, **62**, 499; Orton and Jones, *J. Chem. Soc.*, 1919, **115**, 1055, 1194; Tizard and Marshall, *J. Soc. Chem. Ind.*, 1921, **40**, 20T; Jones, *J. Chem. Soc.*, 1923, **123**, 1374.

[2] Atkins and Wallace, *Biochem. J.*, 1913, **7**, 219.

[3] See, for example, Young, *Fractional Distillation* (Macmillan); or Kuenen, *Verdampfung und Verflüssigung von Gemischen* (Barth), where the subject is fully treated.

tained so long as the two liquid phases are present; the temperature being supposed constant.

In Fig. 32 is given a diagrammatic representation of the two kinds of pressure-concentration curves which have so far been obtained. In the one case, the vapour pressure of the invariant system (at constant temperature) lies higher than the vapour pressure of either of the pure components; a phenomenon which is very generally found in the case of partially miscible liquids, *e.g.* ether and water.[1] Accordingly, by the addition of water to ether, or of ether to water, there is an increase in the *total* vapour pressure of the system.

With regard to the second type, the vapour pressure of the systems with two liquid phases lies between that of the two single components. An example of this is found in sulphur dioxide and water.[2] On adding sulphur dioxide to water there is an increase of the total vapour pressure; but on adding water to liquid sulphur dioxide, the total vapour pressure is diminished.

The case that the vapour pressure of the system with two liquid phases is *less* than that of each of the components is not possible.

With regard to the *partial pressure* of the components, the behaviour is more uniform. The partial pressure of one component is in all cases lowered by the addition of the other component, the diminution being approximately proportional to the amount added. If two liquid phases are present, the partial pressure of the components, as well as the total pressure, is constant, and is the same for both phases. That is to say, in the case of the two liquids, saturated solution of water in ether, and of ether in water, the partial pressure of the ether in the vapour in contact with the one solution is the same as that in the vapour over the other solution.[3]

[1] Konowaloff, *Annalen d. Physik*, 1881, **14**, 219.

[2] Roozeboom, *Z. physikal. Chem.*, 1891, **8**, 526; *Rec. Trav. Chim. Pays.-Bas*, 1884, **3**, 38.

[3] Konowaloff, *Annalen d. Physik*, 1881, **14**, 219. See also Kuenen, *Verdampfung und Verflüssigung von Gemischen* (Barth).

CHAPTER VIII.

SYSTEMS OF TWO COMPONENTS (*Continued*).

C. Equilibrium between Solid and Liquid Phases only.

In the two preceding chapters the behaviour of two-component systems has been considered in those cases where equilibrium existed either between a solid and a gas phase only or between two liquid phases only. It is now proposed to consider the behaviour of two-component systems in which equilibrium exists between a solid and a liquid phase only. Such systems are among the most important in the whole range of heterogeneous equilibria. The interest and importance of the investigation of such systems lie in the determination not only of the conditions for the stable existence of the participating substances, but also of the conditions under which chemical combination (if any) takes place between the two components. From such investigations, also, one may ascertain the nature of the compounds formed and the range of their existence. In all such investigations the Phase Rule becomes of conspicuous value on account of the fact that its principles afford, as it were, a touchstone by which the character of the system can be determined, and that from the form of the equilibrium curves obtained, conclusions can be drawn as to the nature of the interaction between the two components.[1]

I. The Components are Completely Miscible in the Liquid State.

(*a*) *The Pure Components only occur as Solid Phases.*

Since the two components in the liquid state are miscible in all proportions, only one liquid phase will exist, namely, a homogeneous mixture or solution of the two components. Since, also, only the pure components can occur as solid (crystalline) phases, the only

[1] A very large number of systems have been studied by the methods to be described in this and following chapters, and only one or two references can be given here. Complete lists will be found in Landolt-Börnstein, *Physikalisch-chemische Tabellen*, and in *International Critical Tables*. Reference may also be made to Saposchnikoff, *Z. physikal. Chem.*, 1904, **49**, 688; Kremann, *Monatshefte*, 1904, **25**, 1215, 1271, 1311, and following volumes; Menschutkin, *Z. anorgan. Chem.*, 1906, **49**, 34, and following volumes; Kremann, *Anwendung der thermischen Analyse* (Ahrens'sche Sammlung); Scarpa, *Atti. R. Accad. Lincei*, 1913-1915; Kendall, Crittenden, and Miller, *J. Amer. Chem. Soc.*, 1923, **45**, 963.

systems possible are S_1—L, S_2—L, and S_1—S_2—L, where S_1 and S_2 represent the crystalline components, and L the liquid solution.

A system which consists of only two phases, S_1—L or S_2—L will be bivariant, and two of the variables, pressure, temperature and composition, must be given definite values before the system is entirely defined. If the pressure is given a definite value, say atmospheric pressure, then the system will become univariant, or the composition will vary with the temperature; or, if the temperature is fixed, the composition will vary with the pressure. On the other hand, the system S_1—S_2—L is univariant, and if the pressure is fixed, the system will be entirely defined. Under a given pressure, the system S_1—S_2—L can exist only at a single definite temperature, and the composition of the liquid phase will also be definite.[1] If, therefore, the equilibria be represented in a temperature-concentration or temperature-composition diagram, the systems S_1—L and S_2—L will be represented by curves, and the system S_1—S_2—L by a point. We thus obtain an equilibrium diagram such as that shown in Fig. 33. In this diagram, which represents the simplest possible equilibrium diagram for a two-component system in which solid solutions are not formed, the points A and B represent the melting-points of the pure components. Since the freezing-point of a liquid is lowered by dissolving another substance in it, it follows that if a quantity of the component B be dissolved in molten (or liquid) A, the temperature at which solid A will be in equilibrium with the solution will be below the freezing-point of pure A; and the greater the concentration of B in the liquid, the lower will be the temperature at which A can exist in equilibrium with it.

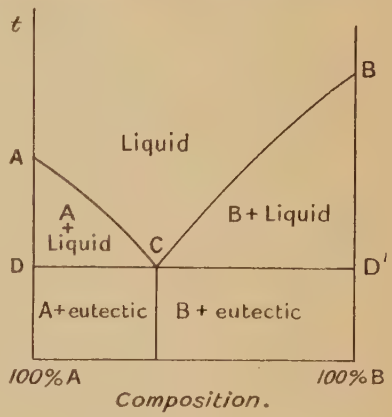


FIG. 33.

For small additions of B, the lowering of the freezing-point of A can be calculated by the simple van't Hoff formula, which may be

[1] The temperature of the eutectic point (p. 104), will, of course, vary with the pressure in accordance with the Clapeyron equation $\frac{dT}{dp} = \frac{T \cdot \Delta v}{Q}$ where Q is the heat absorbed when c gram-molecules of component A and $(1 - c)$ gram-molecules of component B melt to yield the eutectic mixture, and Δv is the change of volume accompanying this change. On the other hand, if the temperature is kept constant, the concentration of the eutectic solution will change with pressure in accordance with the expression $\frac{d \log_e c}{dp} = -\frac{\Delta v}{RT}$, assuming that the vapour of the solution obeys the gas laws. (See Puschin and Grebenschtschikov, *Z. physikal. Chem.*, 1925, **118**, 276; Puschin, *ibid.*, p. 447.)

written in the form, $\frac{dT}{dx_a} = \frac{RT^2}{L_a}$, where x_a is the molar fraction of the component A (the component crystallising as solid phase); T is its melting-point on the absolute scale; R, the gas constant (expressed in heat units); and L_a, the latent heat of fusion of A per gram-molecule. For more concentrated solutions, one may use the expression

$$\log_{10} x_a = \frac{-L_a}{2{\cdot}303 \times 1{\cdot}99}\left(\frac{1}{T} - \frac{1}{T_0}\right),$$

where T is the equilibrium temperature and T_0 is the melting-point of pure A, on the absolute scale.[1] This expression, however, holds strictly only in the case of "ideal" solutions.

The curve AC represents the composition of solutions which are in equilibrium, at different temperatures, with the solid component A; and the curve BC, similarly, the composition of solutions in equilibrium with solid B. At the point C, where the two curves cut, both solid components can exist in equilibrium with a liquid solution of definite composition, corresponding with the point C. Point C gives the conditions of temperature and composition of the liquid phase under which the system S_1—S_2—L can exist in stable equilibrium under constant pressure. This point, as is clear from the diagram, lies *at a lower temperature than the melting-point of either component.* It is, in consequence, called a eutectic point.[2]

At all temperatures lying above the curves AC, BC, the system can exist only as a homogeneous, liquid solution, and at all temperatures below the eutectic horizontal, DD′, only the solid components or mixtures of the solid components can exist as stable systems. When the temperature and composition are represented by a point in the area ACD, mixtures of solid component A can exist along with liquid solutions. Similarly, points in the area BCD′ give the conditions of temperature and composition for the coexistence of solid B and solution.

If a liquid solution having a composition represented by a point lying to the left of the eutectic point C be cooled down, the solid component A will crystallise out (supersaturation supposed excluded) when the temperature reaches the point on the curve AC corresponding with the initial composition of the solution. If the temperature be allowed to fall still further, more and more of the component A will crystallise out, and the composition of the liquid solution will alter in the direction of C. When the composition of the point C is reached, solid B, also, can begin to crystallise out. If one continues to withdraw heat from the system, solid A and solid B will separate out

[1] Washburn and Read, *Proc. Nat. Acad. Sci.*, 1915, 1, 191; Hildebrand, *Solubility* (Chemical Catalog Co.); van Laar, *Z. physikal. Chem.*, 1908, 63, 216; 1908, 64, 257; 1909, 66, 197.

[2] Derived from the Greek εὖ and τηκτός (eu, tēctos) = easy melting (Guthrie, *Phil. Mag.*, 1875 [4], 49, 1; 1884 [5], 17, 462).

together, while *the temperature remains constant.* Since the composition of the solution must also remain constant (point C represents an invariant system when the pressure is constant), it follows that *the components A and B must crystallise out from the eutectic solution in constant proportions.* Although, therefore, the solution having the composition of the eutectic point freezes at constant temperature, the solid which separates out is not a compound but a *mixture* (*or conglomerate*) *of two solid phases.*

On the other hand, if a liquid mixture having a composition represented by a point lying to the right of the eutectic point C be cooled down, the solid component B will separate out, and the composition of the solution will change in the direction of C. When this point is reached, solid A also will crystallise out, and the temperature and composition of the solution will now remain constant while the solid components A and B crystallise out as a eutectic conglomerate.

On cooling down a liquid mixture which has the composition represented by the eutectic point C, no solid will crystallise out until the temperature of the eutectic point is reached. At this temperature the eutectic mixture will separate out.

Polymorphism of Components.—The curves AC and BC, shown in Fig. 33, represent diagrammatically the equilibrium relations which obtain when the pure components crystallise out from the fused or liquid mixture. We have seen, for example, that the solid phase in equilibrium with solutions of composition represented by points on the curve BC is the component B. So long as this solid phase undergoes no change, the curve BC must be a continuous curve, as shown in Fig. 33. If, however, the solid component can exist in enantiotropic, polymorphic forms, the equilibrium curve will show a " break " at the transition point of the crystalline forms, for, at the transition point, there will coexist two solid phases (polymorphic forms) and a liquid phase. At constant pressure, therefore, the system will be invariant. Below the transition point the one crystalline form, and above the transition point the other crystalline form, will exist in equilibrium with solution. At the transition point these two equilibrium curves will cut.

Summing up, it may be said that when two components are completely miscible in the liquid state, and when only the pure components occur as solid phases, the diagram of equilibria between solid and liquid phases will consist of two curves meeting at a eutectic point.

Determination of the Equilibrium Curve.—The method employed for the experimental determination of the equilibrium curve will depend on the nature of the system to be investigated. Where one of the components is a volatile liquid (*e.g.* water) at ordinary temperatures, the composition of the solution may be determined by evaporation of the liquid and weighing of the solid residue. Such systems will receive special consideration later. When both components are solid at ordinary temperatures, the course of the equilibrium

curves can best be established by determining the freezing-points of homogeneous liquid mixtures of different initial composition, or the temperatures at which the solid phase begins to crystallise out from the liquid mixture. (The equilibrium curve is, in consequence, frequently spoken of as the freezing-point curve.) The mapping of the freezing-point curve is facilitated by a study of the " cooling curve." [1]

When a pure substance in the fused state is allowed to cool slowly, and the temperature noted at different times, the graphic representation of the rate of cooling will give a continuous curve, *e.g. ab* in Fig. 34, I. When the freezing-point is reached, solid will begin to separate out (if supercooling is supposed to be absent), and the temperature will remain constant until the liquid has completely solidified. The fall of temperature will then become uniform again (*cd*).

If, however, a solution is allowed to cool slowly, and the cooling curve similarly determined, we shall again obtain a continuous curve, *a'b'* (Fig. 34, II.), so long as the solution is entirely liquid. When, however, a solid phase begins to be formed, heat will be evolved and the rate of cooling will alter. The cooling curve will therefore exhibit

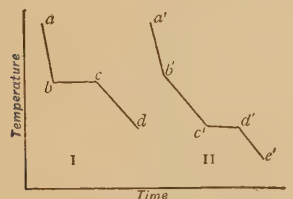


FIG. 34.

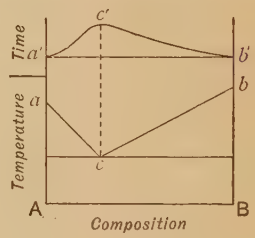


FIG. 35.

a break or change of direction at the freezing-point of the solution (point *b'*). Since the composition of the solution alters with separation of the solid phase, the temperature will not remain constant, but will gradually fall until the eutectic point is reached. A second solid phase is now formed and the system now becomes invariant (supercooling being supposed excluded). The temperature will therefore remain constant until complete solidification has occurred (line *c'd'*). Thereafter, the fall of temperature again becomes uniform (*d'e*). The points *b*, *b'*, and *c'*, at which a " break " occurs in the cooling curve, are called " arrests " or " arrest points," on the cooling curve.

The length of time during which the temperature remains constant at the point *c'*, depends, of course, on the amount of solution which

[1] For practical details and a discussion of the method as applied more especially to mixtures of metals, see Desch, *Metallography* (Longmans); Tammann, *Z. anorgan. Chem.*, 1903, **37**, 303; 1905, **45**, 24. Reference may be made here to the registering pyrometer of Kurnakov, *Z. anorgan. Chem.*, 1904, **42**, 184. See also Plato, *Z. physikal. Chem.*, 1907, **58**, 350; E. Rengade, *Compt. rend.*, 1909, **149**, 782, 990; Friedrich, *Metallurgie*, 1910, **7**, 33; Guye, *J. Chim. phys.*, 1910, **8**, 119; Tsakalotos and Guye, *ibid.*, 1910, **8**, 340. A full account of the method is given by Kremann, *Anwendung der thermischen Analyse* (Ahrens'sche Sammlung).

remains unsolidified when the eutectic point is reached. If, therefore, we take equal amounts of solution having a different initial composition, the period of constant eutectic temperature on the cooling curve will evidently be greatest in the case of the solution having the composition of the eutectic point; and the period will become less and less as we increase the amount of one of the components. The relationship between initial composition of solution and the duration of constant temperature at the eutectic point is represented by the curve *a'c'b'* (Fig. 35).

By noting the temperatures at which " arrests " occur on the cooling curve of different mixtures, it is possible to map out the equilibrium diagram of the system. The cooling curve, moreover, gives valuable information regarding the *nature of the solid phases*. From Fig. 35 it is clear that when the duration of constant eutectic temperature on the cooling curve is plotted against the initial composition of the liquid mixture, a simple curve, with a time maximum at the eutectic composition, is obtained; and when such a curve is obtained it indicates that only the pure components occur as solid phases. This is known as the method of *thermal analysis*.

In some cases the method of thermal analysis is not convenient to use, owing to sluggishness of crystallisation or the tendency of the liquid to supercool. In such cases, the determination of the temperatures of incipient and complete fusion of intimate mixtures of varying composition may be used for the purpose of mapping the equilibrium curves.[1]

It may be pointed out that when the solid components exist in polymorphic forms, the cooling curve will show a line of constant temperature, similar to *c'd'* (Fig. 34) at the transition point. In this case, however, the liquid will not completely solidify, and only a change in the solid phase will take place. When this change is complete, the temperature will again fall until the eutectic point (or other point corresponding to an invariant system) is reached.

Example.—An equilibrium diagram belonging to the class of systems just discussed is given by the system *o*-nitrophenol—*p*-toluidine (Fig. 36).[2] The solid phase in equilibrium with solutions represented by the left-hand branch of the curve is *o*-nitrophenol (m.p. 44·1°); that in equilibrium with the solutions represented by the right-hand branch, is *p*-toluidine (m.p. 43·3°). At the eutectic point (15·6°), these two solid phases can coexist with the liquid phase. This equilibrium curve, therefore, shows that *o*-nitrophenol and *p*-toluidine do not combine with each other.

In connection with this curve, attention may be called to the fact that although the solid produced by cooling the liquid phase at the eutectic point has a composition approximating to that of a compound

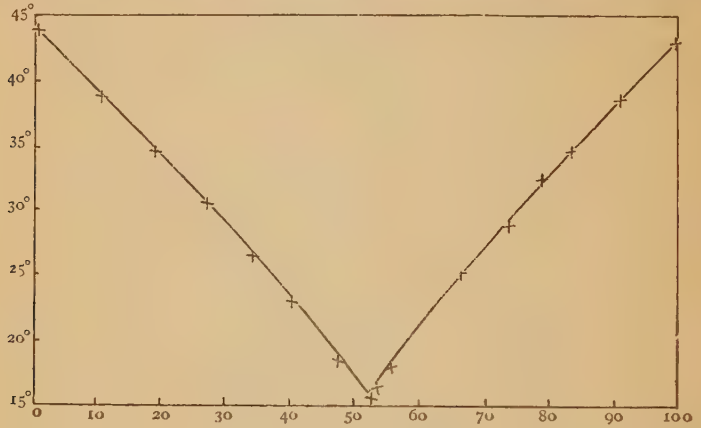
[1] Rheinboldt, *J. pr. Chem.*, 1925 [2], **111**, 242; Rheinboldt and Kircheisen, *ibid.*, 1926 [2], **112**, 187; **113**, 199, 348.

[2] Philip, *J. Chem. Soc.*, 1903, **83**, 821.

of equimolecular proportions of the phenol and toluidine, and a constant melting-point, it is nevertheless a *mixture*. Although, as a rule, the constituents of the eutectic mixture are not present in simple molecular proportions, there is no reason why they should not be so; and it is therefore necessary to beware of assuming the formation of compounds in such cases.[1]

(*b*) *Compounds are Formed with a Congruent Melting-point.*

When two components can form a stable compound possessing a *congruent melting-point*, *i.e.* capable of existing as a solid compound, in equilibrium with a liquid of the same composition, a third equilibrium curve (compound in equilibrium with liquid solution) must be added to the two curves discussed in the preceding section. Moreover,



Molecular percentage of toluidine.

FIG. 36.

since the compound has a definite congruent melting-point, and since this melting-point will be lowered by dissolving in the liquid either of the pure components, it follows that the melting-point of the compound must be a maximum point on the equilibrium curve. The equilibrium diagram, therefore, takes the general form shown in Fig. 37, curve I. A, B, and D are the congruent melting-points of component A, component B, and of the compound $A_x B_y$ respectively. Curve AC gives the composition of liquid mixtures (solutions) of A and B in equilibrium at different temperatures with the component A as solid phase; curve BE gives the composition of solutions in equilibrium with component B as solid phase; and curve CDE gives the composition of solutions in equilibrium with the compound as solid phase. C and E are eutectic points at which eutectic conglomerates

[1] *Cf.* also Paternò and Ampolla, *Gazzetta*, 1897, **27**, 481.

of A and $A_x B_y$ and of B and $A_x B_y$ respectively can coexist in contact with solutions of definite composition. The curve for the compound may occupy a large or a small part of the diagram, and the melting-point, D, of the compound may lie either higher or lower than that of either of the components, or it may have an intermediate position. If more than one compound with congruent melting-point can be formed, a series of curves similar to CDE will be obtained—one for each compound. In each case the maximum point on the curve gives the composition of the compound.

With regard to the form of the curve CDE, it might be thought that since D is the melting-point of a pure substance, and since this melting-point (equilibrium point) will be lowered by addition of a second substance to the liquid phase, the two branches of the curve should not pass continuously one into the other, but *intersect* at the point D. This would be the case if the compound were *completely undissociated* into its components, even in the vapour phase, *e.g.* the compound of pyridine and methyl iodide.[1] When, however, dissociation of the compound into the components takes place in the liquid phase, we are dealing throughout with mixtures of molecules in the liquid phase and the composition of this mixture varies continuously with the temperature. So long, therefore, as the solid phase remains unchanged, the equilibrium curve must be continuous, and the crest of the curve, CDE, will be rounded. The less the degree of dissociation of the compound in the liquid phase, the sharper will be the bend of the curve; and the greater the degree of dissociation, the flatter will the curve become.[2] From the extent of the flattening of the curve, it is possible, with some degree of approximation, to calculate the degree of dissociation of the compound in the fused state.[3]

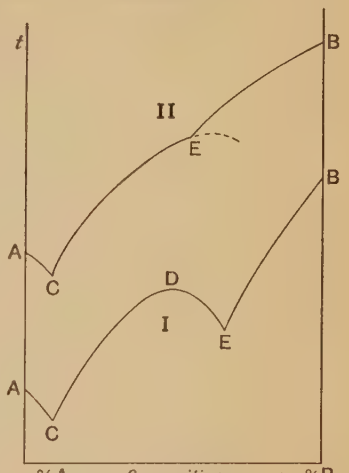


FIG. 37.

The law of mass action applied to the dissociation of the binary compound into its two components, yields the expression

$$\left(\frac{x}{100+x}\right)^2 = K \cdot \left(\frac{100-x}{100+x}\right),$$

[1] Aten, *Proc. K. Akad. Wetensch. Amsterdam*, 1904, **7**, 468.

[2] Kurnakov and Solovev, *Proc. J. Russ. Phys. Chem. Soc.*, 1916, **48**, 1333; Stortenbeker, *Z. physikal. Chem.*, 1892, **10**, 194.

[3] Bancroft, *J. Physical Chem.*, 1899, **3**, 72; Roozeboom and Aten, *Z. physikal. Chem.*, 1905, **53**, 463; Kremann, *Z. Elektrochem.*, 1906, **12**, 259; Findlay and Hickmans, *J. Chem. Soc.*, 1907, **91**, 905; Kendall and Booge, *J. Chem. Soc.*, 1925, **127**, 1768; Ross and Somerville, *J. Chem. Soc.*, 1926, p. 2770.

where x is the percentage number of molecules of each of the components produced by the dissociation, and $100 + x$ is the total number of molecules. From this the value of K can be calculated for any given value of x, that is, for any given degree of dissociation. If, now, an excess of a gram-molecules of one of the components is added, the dissociation will be altered in approximate accordance with the expression

$$\frac{x'(x'+a)}{(100+x'+a)^2} = \mathrm{K} \cdot \left(\frac{100-x'}{100+x'+a}\right).$$

From this the new value of x can be calculated. One is thus enabled to calculate the actual number of molecules which have a depressing effect on the freezing-point. If, further, the value of the molecular depression of the freezing-point is known, or the latent heat of fusion of the component which crystallises out, the course of the freezing-point curve can be calculated for mixtures of different composition and for any assumed value of dissociation (p. 104). It only remains to compare the actual freezing-point curve with the curves calculated for different degrees of dissociation.

By dropping perpendiculars from the points C, D, and E to the composition axis, and drawing eutectic horizontals through the points C and E, the diagram is divided up into areas, similar to those shown in Fig. 33. Below the eutectic horizontal through C, and to the left of the perpendicular from D, mixtures of solid A and eutectic or solid compound and eutectic can exist; and similarly, below the eutectic horizontal through E and to the right of the perpendicular from D, mixtures of solid B and eutectic and of solid compound and eutectic can exist. At temperatures above the eutectic horizontals, and below the equilibrium curve, mixtures of solid A and solution, solid compound and solution, and solid B and solution, can exist.

The Indifferent Point.—A two-component system consisting of only two phases, a solid and a liquid, possesses, according to the Phase Rule, a variability of two. We have, however, just learned that a compound with a congruent melting-point may be formed in a two-component system, and that this melting-point varies only with the pressure. In other words, at the congruent melting-point of a compound of two components, the two-phase system, solid—liquid, is not bivariant, but univariant. *The variability of the system has therefore been diminished.*

A point such as that to which reference has just been made, which represents the special behaviour of a system of two (or more) components in which two phases become identical in composition, is known as an *indifferent point;* [1] and it has been shown [2] that, under a given pressure, the temperature in the indifferent point is the *maximum* or *minimum* temperature possible at the particular pressure [3] (*cf.* critical

[1] Duhem, *J. Physical Chem.*, 1898, **2**, 31.

[2] Gibbs, *Trans. Conn. Acad.*, **3**, 155; Saurel, *J. Physical Chem.*, 1901, **5**, 35.

[3] In the case of the fusion of a compound of two components with formation of a liquid phase of the same composition, the temperature is a maximum; in the case of liquid mixtures of constant boiling-point, the temperature may be a minimum.

solution temperature). At such a point a system loses one degree of freedom, or behaves like a system of the next lower order.

Determination of the Composition of a Compound by Thermal Analysis.—It has already been pointed out that when one plots the duration of constant eutectic temperature on the cooling curve against the initial composition of the liquid mixture, a curve is obtained which shows a maximum when the initial composition is that of the eutectic point. When a compound possessing a congruent melting-point is formed, it behaves like a pure component. If, therefore, the initial composition of the solution is the same as that of the compound, no eutectic solution will be obtained; and the cooling curve will have the form shown in Fig. 34, I. If, therefore, we represent graphically the relation between the initial composition of the solution and the duration of constant temperature at the eutectic point (*c'd'* in Fig. 34, II.), in the case where a compound with definite melting-point is formed, a diagram is obtained such as shown in Fig. 38. The two maxima on the time-composition curve represent eutectic points, and the minima, *a'*, *b'*, *e'*, pure substances. The position of *e'* gives the composition of the compound. When a series of compounds is formed, then for each compound a minimum is found on the time-composition curve.

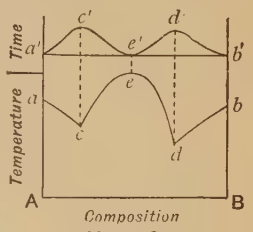


FIG. 38.

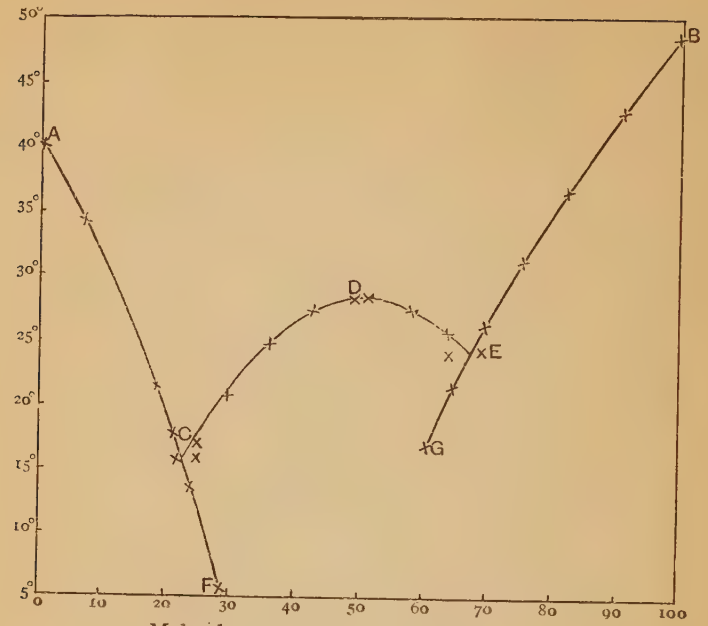
Examples.—On determining the freezing-points of mixtures of phenol and α-naphthylamine, a curve (Fig. 39) is obtained of the type shown in Fig. 37, curve I., indicating the formation of a compound.[1]

Phenol freezes at 40·4°, but the addition of α-naphthylamine lowers the freezing-point as represented by the curve AC. At C (16·0°) the compound C_6H_5OH, $C_{10}H_7NH_2$ is formed, and the system becomes invariant. On increasing the amount of the amine, the temperature of equilibrium rises, the solid phase now being the compound. At D, the curve passes through a maximum (28·8°), at which the solid and liquid phases have the same composition. This is the (congruent) melting-point of the compound. Further addition of the amine lowers the temperature of equilibrium, until at E solid α-naphthylamine separates out, and a second eutectic point (24·0°) is obtained. BE is the freezing-point curve of α-naphthylamine in presence of phenol, the freezing-point of the pure amine being 48·3°.

On account of the great sluggishness with which the compound of phenol and α-naphthylamine crystallises out from solution, it was found possible to follow the freezing-point curves of phenol and of the amine to temperatures considerably below the eutectic points, as shown by the curves CF and EG.

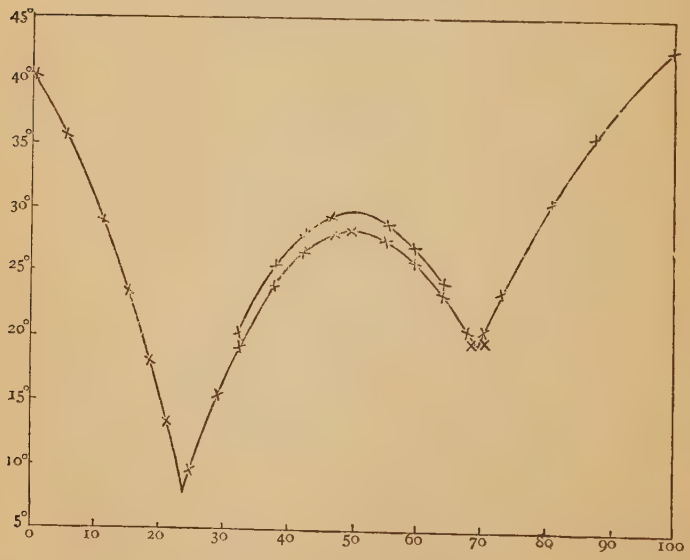
Phenol can also combine with *p*-toluidine in equimolecular proportions; and this compound is of interest, from the fact that it

[1] Philip, *J. Chem. Soc.*, 1903, **83**, 821.



Molecular percentage of α-naphthylamine.

FIG. 39.



Molecular percentage of toluidine.

FIG. 40.

exists in two crystalline forms, melting at 28·5° and 30°. Each of these forms must have its own equilibrium curve, and it was found that the intermediate portion of the freezing-point curve was duplicated, as shown in Fig. 40.[1]

On cooling down mixtures (solutions) of fused phenol (A) and α-naphthylamine (B) having a composition represented by a point lying between A and C (Fig. 39), pure phenol will crystallise out when the temperature has fallen to a point on the curve AC. On further cooling, the composition of the solution will alter in the direction of C, and when this point is reached the compound D (C_6H_5OH, $C_{10}H_7NH_2$) will also crystallise out. The eutectic conglomerate in this case is, therefore, a mixture of phenol and of the compound D. From solutions having a composition represented by any point between C and D, compound D will crystallise out on cooling, and the composition of the solution will alter in the direction C. On reaching this temperature, the solution will again deposit the eutectic mixture of phenol and compound D. Similarly, when the liquid mixture has a composition lying between that of the points D and E, the compound D will first separate out on cooling, and then the conglomerate D and α-naphthylamine, while from solutions of composition between E and B, solid α-naphthylamine will crystallise out until the composition has changed to that of the point E. The eutectic conglomerate, α-naphthylamine and the compound D, will then separate out together. From solutions having the composition of the point D, only the compound will crystallise out from beginning to end.

(*c*) *Compounds are Formed with an Incongruent Melting-point.*

When a compound is formed which undergoes decomposition with formation of another solid phase at a temperature below the congruent melting-point of the compound, the equilibrium diagram assumes the general form shown in Fig. 37, curve II. This corresponds to the case where a compound can exist only in contact with solutions containing excess of one of the components. The metastable continuation of the equilibrium curve for the compound is indicated by the dotted line, the summit of which would be the congruent melting-point of the compound. Before this temperature is reached, however, the solid compound ceases to be stable, and undergoes decomposition into another solid phase [2] and liquid at the point E. Since the composition of the liquid formed is not the same as that of the compound, this point is spoken of as an *incongruent melting-point*. This point, therefore, represents the limit of the existence of the compound $A_x B_y$ under the particular constant pressure which is assumed. If a series of compounds can be formed none of which possesses a congruent

[1] Philip, *loc. cit.* Compare curves for iodine monochloride (Fig. 83, p. 194).

[2] This solid phase may be another compound, or it may be a pure component. It is the latter case which is represented in Fig. 37.

melting-point, then a series of curves will be obtained which do not exhibit a temperature maximum, and there will be only one eutectic point. The limits of existence of each compound (or the incongruent melting-point) will in each case be marked by a break in the curve.

Determination of the Composition of the Compound by Thermal Analysis.—Since the compound does not have a congruent melting-point, it is clear that the temperature-maximum on the equilibrium curve will not be reached. It will not, therefore, be possible to determine the composition of the compound from the freezing-point or equilibrium curve alone. Recourse may, however, be had to the method of thermal analysis.

When the compound formed has no congruent melting-point, the thermal analysis diagram obtained is like that shown in Fig. 41. If we start with a solution, the composition of which is represented by a point between *d* and *b*, then, on cooling, component B will separate out first, and the temperature will fall until the point *d* is reached. The temperature then remains constant until the component B, which has separated out, is converted into the compound. After this the temperature again falls, until it again remains constant at the eutectic point *c*. In the case of the first arrest point, the period of constant temperature is greatest when the initial composition of the solution is the same as that of the compound; and it becomes shorter and shorter with increase in the amount of either component. In this way we obtain the time-composition curve $b'e''d'$, of which the maximum point e'' gives the composition of the compound.

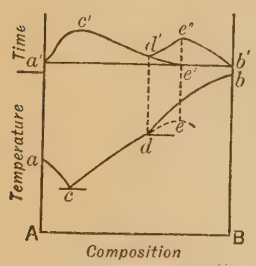


FIG. 41.

On the other hand, the period of constant temperature for the eutectic point *c* is greatest in the case of solutions having the same initial composition as the eutectic mixture; and it decreases the more the initial composition approaches that of the pure component *a* or the compound *e*. In this way we obtain the time-composition curve $a'c'e'$. Here also the point e' represents the composition of the compound. We see, therefore, that from the graphic representation of the freezing-point curve, and from the duration of the temperature-arrests on the cooling curve, for solutions of different initial composition, it is possible, without having recourse to analysis, to decide what solid phases are formed, and what is their composition.

Example.—An example of the type of system just discussed is found in the case of benzene and picric acid.[1] These two susbtances combine, in equimolecular proportions, to form a compound which, however, can exist only in contact with solutions *containing excess of benzene* (Fig. 42). When the temperature is raised a point (K) is

[1] Kuriloff, *Z. physikal. Chem.*, 1897, **23**, 676.

reached at which the compound melts with separation of solid picric acid. The point K is, therefore, an incongruent melting-point; analysis, however, showed that the composition of the solution at this point is very nearly that of the compound $C_6H_2(NO_2)_3OH$, C_6H_6, so that the melting-point of the compound can almost be reached. The tusion of the compound of benzene and picric acid with separation of fhe latter is analogous to the (partial) fusion of Glauber's salt with separation of anhydrous sodium sulphate.

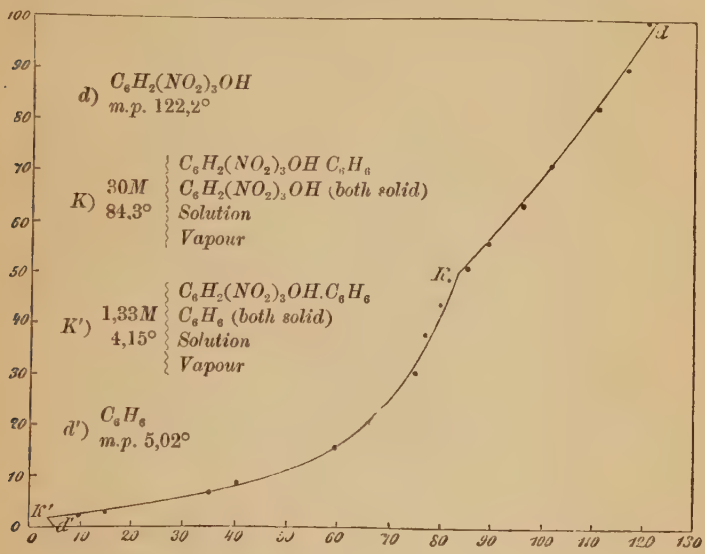


FIG. 42.

(d) Solid Solutions or "Mixed Crystals" are Formed.

The introduction by van't Hoff of the term "solid solution" resulted from the discovery of a number of deviations from the Raoult-van't Hoff law for the depression of the freezing-point by dissolved substances. In all cases, the depression was too small; in some instances, indeed, the freezing-point was raised. To explain these irregularities, van't Hoff assumed that the dissolved substance crystallised out along with the solid solvent; and he showed how this would account for the deviations from the law of the depression of the freezing-point, which had been developed on the assumption that only the pure solvent crystallises out from the solution.[1]

The "mixed crystals" which were thus obtained, and which van't Hoff called dilute solid solutions, showed great resemblance in their behaviour to ordinary liquid solutions, and obeyed the laws applicable

[1] *Z. physikal. Chem.*, 1890, **5**, 322.

to these. These laws, however, can no longer be applied in the case of the concentrated solid solutions formed by the crystallisation together of isomorphous substances, and known as isomorphous mixtures. Indeed, it has been contended [1] that these isomorphous mixtures should not be considered as solid solutions at all, but this is a position which can now no longer be maintained. For it has been shown [2] that *diffusion*, a process regarded as characteristic of the gaseous state and the state of solution, takes place not only in the case of crystalline metals, but also in the case of crystalline salts, *e.g.* sodium chloride—potassium chloride, mercuric bromide—mercuric iodide, and of organic compounds, such as azobenzene—dibenzyl, azobenzene—stilbene. Moreover, the heat of solution of "mixed crystals" is not equal to the sum of the heats of solution of the component salts,[3] and when mixed crystals of gold and copper, or of gold and silver, are treated with reagents which are solvents for one of the components, they do not behave as if they were heterogeneous mixtures.[4] Finally, X-ray examination of "mixed crystals" of potassium chloride and potassium bromide, of potassium bromide and ammonium bromide, etc., has shown that they behave as a single entity, and not as if they were composed of thin laminæ of the individual salts.[5] In the crystal lattice of the mixed crystal, the "vicarious" elements replace each other atom for atom.

No essential distinction, therefore, can be drawn between crystalline solid solutions and "isomorphous mixtures"; and since the term "mixed crystal" is apt to suggest heterogeneity and so to introduce confusion, the term *solid solution* is preferable and will be employed here.[6]

Crystalline solid solutions can be formed either by sublimation [7] or from a liquid phase; and in the latter case the solid solution can be deposited either from solution in a common solvent or from a mixture of the fused components. In this method of formation, which alone will be discussed in the present chapter, we are dealing with the fusion curves of two substances, where, however, the liquid solution is in equilibrium not with one of the pure components, but with a crystalline solid solution. The simple scheme (Fig. 33, p. 103) which was obtained

[1] Küster, *Z. physikal. Chem.*, 1895, **17**, 367; Bodländer, *Jahrb. Min. Beil.-Bd.*, 1898-99, **12**, 92; Lehmann, *Annalen d. Physik*, 1894, **51**, 67; Ružička, *Z. physikal. Chem.*, 1910, **72**, 381; Von Weimarn, *Kolloid-Z.*, 1910, **7**, 35.

[2] Bruni and Meneghini, *Atti R. Accad. Lincei*, 1911 [5], **20**, i. 671, 927 (or see Bruni, *Mem. Accad. Lincei*, 1912, **9**, 40); Quercigh, *Atti Accad. Sci. Napoli*, 1914 [2], **16**, Nr. 7; Sirovich and Cartoceti, *Gazzetta*, 1922, **52**, i. 436; Tammann, *Z. anorgan. Chem.*, 1919, **107**, 1; Desch, *Brit. Assoc. Reports*, 1912, p. 348.

[3] Bruni and Meneghini, *Atti Ist. Veneto*, 1911, **71**, II. 195.

[4] Tammann, *Nachr. Ges. Wiss. Göttingen*, 1916, p. 199.

[5] Vegard and Schjelderup, *Physikal. Z.*, 1917, **18**, 93; Vegard, *Z. Physik*, 1921, **5**, 393.

[6] For a general survey of this subject, see Bruni, *Ueber Feste Lösungen* (Ahrens'sche Sammlung); Bodländer, *Jahrb. Min. Beil.-Bd.*, 1898-99, **12**, 92; Bruni, *Chemical Reviews*, 1925, **1**, 345; Bain, *Chem. and Met. Eng.*, 1923, **28**, 21.

[7] Bruni and Padoa, *Atti Accad. Lincei*, 1902 [5], **11**, 1, 565.

in the case of two components which crystallise out in the pure state, is no longer sufficient in the case of the formation of solid solutions. With the help of the Phase Rule, however, the different possible systems can be classified; and examples of the different cases predicted by the Phase Rule have also been obtained by experiment.

We shall now consider briefly the formation of solid solutions by isomorphous substances; the consideration of the formation of solid solutions of isodimorphous substances will, on account of the complexity of the relationships, not be undertaken here.[1]

Formation of Solid Solutions from Mixtures of the Fused Components.

For the purpose of representing the relationships found here we shall employ a temperature-concentration diagram,[2] in which the ordinates represent the temperature and the abscissæ the concentration of the components. Since there are two solutions, the liquid and the solid, and since the concentration of the components in these two phases is not, in general, the same, two curves will be required for each system, one relating to the liquid phase, the other relating to the solid. The temperature at which solid begins to be deposited from the liquid solution will be called the *freezing-point* of the mixture, and the temperature at which the solid solution just begins to liquefy will be called the *melting-point* of the solid solution. The temperature-concentration curve for the liquid phase will therefore be the freezing-point curve; that for the solid solution, the melting-point curve. The latter will be represented by a dotted line. These curves are also very generally referred to as the "liquidus" and the "solidus" curve respectively.

(*i*) *The Two Components can Form an Unbroken Series of Solid Solutions.*

Since, as has already been pointed out (p. 116), a solid solution constitutes only one phase, it is evident that if the two components are miscible with each other in all proportions in the solid state, there can never be more than one solid phase present, viz. a solid solution of varying composition. If the components are completely miscible

[1] Roozeboom, *Z. physikal. Chem.*, 1899, **30,** 385; Bruni, *Rend. Accad. Lincei*, 1898, **2,** 138, 347. For the formation and transformation of liquid "mixed crystals," see A. C. de Kock, *Z. physikal. Chem.*, 1904, **48,** 129; Ada Prins, *ibid.*, 1909, **67,** 688; 1911, **75,** 681; Smits and Lobry de Bruyn, *Proc. K. Akad. Wetensch. Amsterdam*, 1913, **16,** 557; Vorländer and Gahren, *Ber.*, 1907, **40,** 1966; Walter, *ibid.*, 1925, 58, B, 2303.

[2] In discussing the various systems which may be obtained here, Roozeboom (*Z. physikal. Chem.*, 1899, **30,** 385) made use of the variation of the thermodynamic potential (p. 13) with the concentration. In spite of the advantages which such a treatment affords, the temperature-concentration diagram has been adopted as being more readily understood and as more suitable for an elementary discussion of the subject. For a general mathematical discussion of the different systems possible, see also J. J. van Laar, *Z. physikal. Chem.*, 1908, **63,** 216; **64,** 257; 1909, **66,** 197.

in the solid state, they will also be completely miscible in the liquid state, and there can therefore be only one liquid phase. The system can at no point become invariant, because there can never be more than three phases present.[1] When, therefore, the two components form a continuous series of solid solutions, the equilibrium curve must also be continuous. Of these systems three types are found :—

(*a*) *The freezing-points of all mixtures lie between the freezing-points of the pure components* (Curve I., Fig. 43).

Examples.—This type of curve is represented by the solid solutions of naphthalene and β-naphthol.[2] The addition of β-naphthol to naphthalene raises the freezing-point of the latter, and the rise is directly proportional to the amount of naphthol added. The freezing-point curve is therefore a straight line joining the melting-points of the two components. This behaviour, however, is rather exceptional, the freezing-point curve lying generally above, sometimes also below, the straight line joining the melting-points of the pure components. Thus the freezing-point curve of mixtures of α-monochlorocinnamic aldehyde and α-monobromocinnamic aldehyde [3] lies above the straight line joining the melting-points of the pure components (31·22° and 69·56°), as is evident from the following table :—

Molecules of bromo-cinnamic aldehyde in 100 mols. of mixture.	Freezing-point.	Deviation from straight line.
0·00	31·22°	—
10·48	37·28°	2·04°
21·91	43·12°	3·50°
30·07	46·80°	4·05°
45·04	52·94°	4·45°
62·16	58·82°	3·77°
82·98	65·07°	2·03°
93·50	67·91°	0·84°
100·00	69·56°	—

Melting-point Curve.—This curve, like the freezing-point curve, must also be continuous, and the melting-points of the different solid solutions will lie between the melting-points of the pure components. This is represented by the dotted line in Fig. 43, I. The relative position of the two curves, which can be deduced with the help of thermodynamics and also by experimental determination, is found in all cases to be in accordance with the following rule : At any given tempera-

[1] The three phases will be solid solution, liquid solution, vapour. For the present the vapour phase will be considered as being absent, and the systems will be regarded as being under constant atmospheric pressure. Under these conditions two phases (solid and liquid) will constitute a univariant system. The composition will vary with the temperature.

[2] Küster, *Z. physikal. Chem.*, 1895, **17**, 360 ; Miers and Isaac, *J. Chem. Soc.*, 1908, **93**, 927.

[3] Küster, *Z. physikal. Chem.*, 1891, **8**, 589.

ture, *the concentration of that component by the addition of which the freezing-point is depressed, is greater in the liquid than in the solid phase ;* or, conversely, *the concentration of that component by the addition of which the freezing-point is raised, is greater in the solid than in the liquid phase.* An illustration of this rule is afforded by the two substances chloro- and bromo-cinnamic aldehyde already mentioned. As can be seen from the above table, the addition of chlorocinnamic aldehyde lowers the melting-point of the bromo-compound. In accordance with the rule, therefore, the concentration of the chloro-compound in the liquid phase must be greater than in the solid phase ; and this was found experimentally. At a temperature of 49·44°, the liquid contained 58·52 per cent., the solid only 52·57 per cent. of the chlorocinnamic aldehyde.

From this it will also be clear that on cooling a fused mixture of two substances capable of forming solid solutions, the temperature of

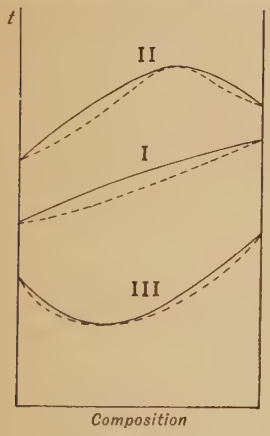


FIG. 43.

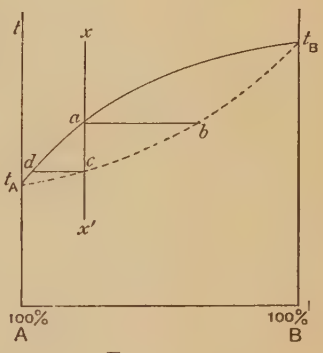


FIG. 44.

solidification will not remain constant during the separation of the solid ; nor, on the other hand, will the temperature of liquefaction of the solid solution be constant. Thus, for example, if a liquid solution of two components, A and B, having the composition represented by the point *x* (Fig. 44), is allowed to cool, the system will pass along the line *xx'*. At the temperature of the point *a*, a solid solution will be deposited, the composition of which will be that represented by *b*. As the temperature continues to fall, more and more solid will be deposited ; and since the solid phase is relatively rich in the component B, the liquid will become relatively poorer in this. The composition of the liquid solution will therefore pass along the curve *ad*, the composition of the solid solution at the same time passing along the curve *bc ;* at the point *c* the liquid will solidify completely.[1]

[1] It should be remarked that the behaviour described here will hold strictly only when the solid solution undergoes change (by diffusion) sufficiently rapidly to be

Conversely, if a solid solution of the composition and at the temperature x' is heated, liquefaction will begin at the temperature c, yielding a liquid of the composition d. On continuing to add heat, the temperature of the mass will rise, more of the solid will melt, and the composition of the two phases will change as represented by the curves da and cb. When the temperature has risen to a, complete liquefaction will have occurred. The process of solidification or of liquefaction is therefore extended over a temperature interval ac.

Even when the freezing-point curve is a straight line joining the melting-points of the pure components, the melting-point curve will not necessarily coincide with the freezing-point curve, although it may approach very near to it; complete coincidence can take place only when the melting-points of the two components are identical. An example of this will be given later (p. 134).

It may be noted that since there can never be more than two phases present (vapour being absent and the pressure constant), the system cannot become invariant. Consequently, when one plots the rate of cooling against time, the cooling curve will show a break at the temperature at which solid solution begins to separate out, and also at the point at which complete solidification has taken place, but there will be no line of constant temperature such as is shown in Fig. 34, curve II. (p. 106). The second break is by no means sharp, and generally takes the form of a flexure in the curve.

(*b*) *The freezing-point curve passes through a maximum* (Curve II., Fig. 43).

This curve exhibits the greatest degree of contrast with the freezing-point curve which is obtained when the pure components crystallise out. For, since the curve passes through a maximum, it is evident that the freezing-point of each of the components must be *raised* by the addition of the other component.

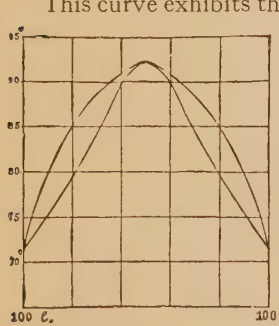


Fig. 45.

Example.—Very few cases belonging to this type are known. The best example is found in the freezing-point curve of mixtures of *d*- and *l*-carvoxime[1] ($C_{10}H_{14}N \cdot OH$). The freezing-points and melting-points of the different mixtures of *d*- and *l*-carvoxime are given in the following table, and represented graphically in Fig. 45 :—

always in equilibrium with the liquid. This, however, is not always the case (see Reinders, *Z. physikal. Chem.*, 1900, **32**, 494; van Wyk, *Z. anorgan. Chem.*, 1905, **48**, 25), and complete solidification will not in this case take place at the temperature corresponding with the line *dc* in Fig. 44, but only at a lower temperature. See also Tammann, *Z. physikal. Chem.*, 1898, **26**, 314; von Lepkowski, *Z. anorgan. Chem.*, 1908, **59**, 285. For a study of the spontaneous crystallisation of solid solutions, see Miers and Isaac, *J. Chem. Soc.*, 1908, **93**, 927; F. Isaac, *Proc. Roy. Soc.*, 1913, A, **88**, 205.

[1] Adriani, *Z. physikal. Chem.*, 1900, **33**, 469.

Per cent. of *d*-carvoxime.	Per cent. of *l*-carvoxime.	Freezing-point.	Melting-point.
100	0	72·0°	72·0°
99	1	72·4°	—
98	2	73·0°	—
95	5	75·4°	73·0°
90	10	79·0°	75·0°
80	20	84·6°	80·0°
70	30	88·2°	85·0°
60	40	90·4°	—
50	50	91·4°	91·4°
25	75	86·4°	82·0°
8	92	77·4°	—
1	99	72·4°	—
0	100	72·0°	72·0°

In this figure, the melting-point curve, *i.e.* the temperature-concentration curve for the solid solutions, is represented by the lower curve. Since the addition of the lævo-form to the dextro-form raises the melting-point of the latter, the concentration of the lævo-form (on the right-hand branch of the curve) must, in accordance with the rule given, be greater in the solid phase than in the liquid. Similarly, since addition of the dextro-form raises the melting-point of the lævo-form, the solid phase (on the left-hand branch of the curve) must be richer in dextro- than in lævo-carvoxime. At the maximum point, the melting-point and freezing-point curves touch ; at this point, therefore, the composition of the solid and liquid phases must be identical. It is evident, therefore, that at the maximum point the liquid will solidify, and the solid will liquefy completely without change of temperature ; and, accordingly, a solid solution of the composition represented by the maximum point will exhibit a definite melting-point, and will in this respect behave like a simple substance.

(*c*) *The freezing-point curve passes through a minimum* (Curve III., Fig. 43).

In this case, as in the case of those systems where the pure components are deposited, a minimum freezing-point is obtained. In the latter case, however, there are two freezing-point curves which intersect at a eutectic point ; in the case where mixed crystals are formed there is only one continuous curve. On one side of the minimum point the liquid phase contains relatively more, on the other side relatively less, of the one component than does the solid phase ; while at the minimum point the composition of the two phases is the same. At this point, therefore, complete solidification and complete liquefaction will occur without change of temperature, and the solid solution will accordingly exhibit a definite melting-point.[1]

[1] The solid solutions may, on cooling, separate into two series of solid solutions, and, finally, into the separate salts, p. 126. See van Laar, *Z. physikal. Chem.*, 1908, **63**, 215 ; 1908, **64**, 257 ; Jänecke, *ibid.*, 1915, **90**, 296.

Example.—As an example of this there may be taken the solid solutions of mercuric bromide and iodide.[1] Mercuric bromide melts at 236·5°, and mercuric iodide at 255·4°. The solid solution of definite constant melting-point (minimum point) contains 59 mols. per cent. of mercuric bromide, the melting-point being 216·1°.

FIG. 46.

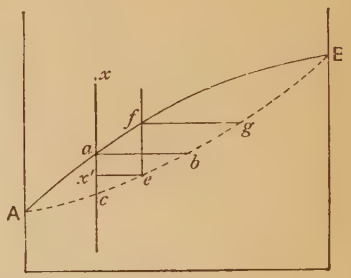


FIG. 47.

The numerical data are contained in the following table, and represented graphically in Fig. 46 :—

Mols. per cent. of $HgBr_2$.	Freezing-point.	Melting-point.
100	236·5°	236°
90	228·8°	226°
80	222·2°	219°
70	217·8°	217°
65	216·6°	216°
60	216·1°	215·5°
55	216·3°	216°
50	217·3°	216°
40	221·1°	218°
30	227·8°	223°
20	236·2°	231°
10	245·5°	242°
0	255·4°	254°

The system KNO_3—$NaNO_3$, similarly, forms a continuous series of solid solutions with a minimum point at 225·7°, the composition being 55 per cent. KNO_3.[2]

Fractional Crystallisation of Solid Solutions.—With the help of the diagrams already given it will be possible to predict what will be the result of the fractional crystallisation of a fused mixture of two substances which can form solid solutions. Suppose, for example, a fused mixture of the composition x (Fig. 47) is cooled down ; then,

[1] Reinders, *Z. physikal. Chem.*, 1900, **32**, 494 ; Losana, *Gazzetta*, 1926, **56**, 301.
[2] Briscoe and Madgin, *J. Chem. Soc.*, 1923, **123**, 1608.

as we have already seen, when the temperature has fallen to *a*, a solid solution of composition *b* is deposited. If the temperature is allowed to fall to *x'*, and the solid then separated from the liquid, the solid solution so obtained will have the composition represented by *e*. If, now, the solid solution *e* is completely fused and the fused mass allowed to cool, separation of solid will occur when the temperature has fallen to the point *f*. The solid solution which is deposited has now the composition represented by *g*, *i.e. it is richer in B than the original solid solution*. By repeating this process, the composition of the successive crops of solid solutions which are obtained approximates more and more to that of the pure component B, while, on the other hand, the composition of the liquid phase produced tends to that of pure A. By a systematic and methodical repetition of the process of fractional crystallisation, therefore, a *practically* complete separation of the components can be effected; a perfect separation is theoretically impossible.

From this it will be readily understood that in the case of substances the freezing-point of which passes through a maximum, fractional crystallisation will ultimately lead to a solid solution having the composition of the maximum point, while the liquid phase will more and more assume the composition of either pure A or pure B, according as the initial composition was on the A side or the B side of the maximum point. In those cases, however, where the curves exhibit a minimum, the solid phase which separates out will ultimately be one of the pure components, while a liquid phase will finally be obtained which has the composition of the minimum point.

(*ii*) *The Two Components do not Form a Continuous Series of Solid Solutions.*

This case corresponds to that of the partial miscibility of liquids. The solid component A can "dissolve" the component B until the concentration of the latter in the solid solution has reached a certain value. Addition of a further amount of B will not alter the composition of the solid solution, but there will be formed a second solid phase consisting of a solution of A in B. At this point the four phases, solid solution containing excess of A, solid solution containing excess of B, liquid solution, vapour, can coexist; this will therefore be an invariant point. The temperature concentration curves will therefore no longer be continuous, but will exhibit a break or discontinuity at the point at which the invariant system is formed.[1]

(*a*) *The freezing-point curve exhibits a transition point* (Curve I., Fig. 48).

As is evident from the figure, addition of B raises the melting-point

[1] For relations between miscibility of solids and chemical constitution, see Vanstone, *J. Chem. Soc.*, 1909, **95**, 591; 1913, **103**, 1826; Pascal, *Bull. Soc. Chim. France*, 1914, **15**, 451.

of A, and, in accordance with the rule previously given, the concentration of B in the solid solution will be greater than in the liquid solution. This is represented in the figure by the dotted curve AD. On the other hand, addition of A lowers the melting-point of B, and the two curves BC and BE are obtained for the liquid and solid phases respectively. At the temperature of the line CDE the liquid solution of the composition represented by C is in equilibrium with the two

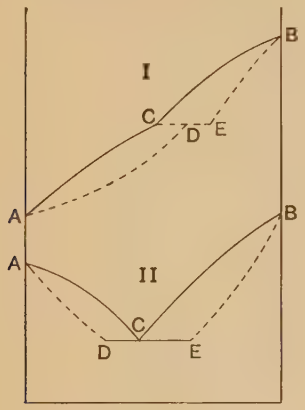


FIG. 48.

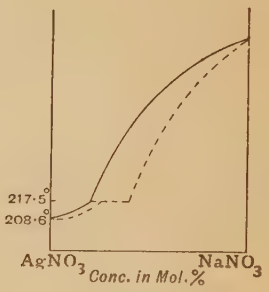


FIG. 49.

different solid solutions represented by D and E. At this temperature, therefore, the *tc*-curve for the solid phase exhibits a discontinuity; and, since the solid phase undergoes change at this point, the freezing-point curve must show a break (p. 105).

Example.—Curves of the form given in Fig. 48, I., have been found experimentally in the case of silver nitrate and sodium nitrate.[1] The following table contains the numerical data, which are also represented graphically in Fig. 49 :—

Molecules $NaNO_3$ per cent.	Freezing-point.	Melting-point.
0	208·6°	208·6°
8	211·4°	210°
15·06	215°	212°
19·46	217·2°	214·8
21·9	222°	215°
26	228·4°	216·5°
29·7	234·8°	217·5°
36·2	244·4°	217·5°
47·3	259·4°	237·6°
58·9	272°	257°
72	284°	274°
100	308°	308°

[1] Hissink, *Z. physikal. Chem.*, 1900, **32**, 542.

The temperature of the transition point is 217·5°; at this point the liquid contains 19·5, and the two conjugate solid solutions 26 and 38 molecules of sodium nitrate per cent. respectively.

(*b*) *The freezing-point curve exhibits a eutectic point* (Curve II., Fig. 48).

In this case the freezing-point of each of the components is lowered by the addition of the other, until at last a point is reached at which the liquid solution solidifies to a mixture or conglomerate of two solid solutions.

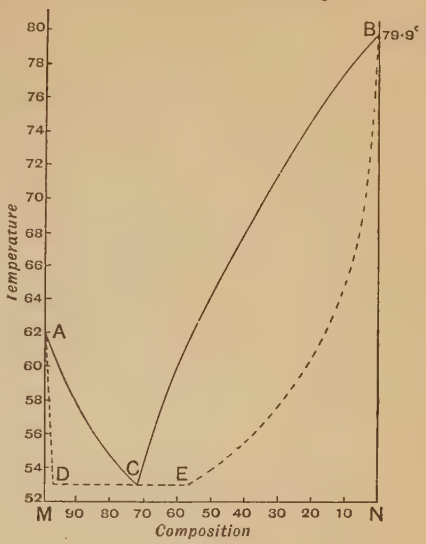


FIG. 50.

Examples. — Curves belonging to this class have been obtained in the case of potassium and thallium nitrates [1] and of naphthalene and monochloracetic acid.[2] The data for the latter are given in the following table and represented in Fig. 50 :—

Temperature.	Liquid solution.		Solid solution.	
	Per cent. naphthalene.	Per cent. acid.	Per cent. naphthalene.	Per cent. acid.
62°	—	100·0	—	100
60°	4·0	96·0	1·7	98·3
55°	21·0	79·0	2·1	97·9
53·5°	29·4	70·0	—	—
55°	31·3	68·7	59·6	40·4
60°	42·4	57·6	80·3	19·7
65°	53·3	46·7	89·2	10·8
70°	69·7	32·3	95·4	4·6
75°	84·4	15·6	96·6	3·4
79·9°	100	—	100	—

At the eutectic point the liquid solution is in equilibrium with two different solid solutions, the composition of which is represented by D and E respectively. If, therefore, a fused mixture containing the two components A and B in the proportions represented by C is cooled down, it will, when the temperature has reached the point C, solidify completely to a *conglomerate* of two solid solutions, D and E.

[1] Van Eyk, *Z. physikal. Chem.*, 1899, **30**, 430.
[2] Cady, *J. Physical Chem.*, 1899, **3**, 127.

Changes in Solid Solutions with the Temperature.—In the case of the different types of systems represented in Fig. 43, a homogeneous liquid solution of the two components will exist at temperatures above the freezing-point curve, a homogeneous solid solution at temperatures below the melting-point curve, while at any point between the freezing-point and melting-point curves the mixture will separate into a solid phase and a liquid phase. In the case, however, of the two types shown in Fig. 48, the relationships are somewhat more complicated. As before, the area above the freezing-point curve gives the conditions under which homogeneous liquid solutions can exist; but below the melting-point curve two different solid solutions can coexist. This will be best understood from Figs. 51 and 52. D and E represent, as we have seen, the composition of the two solid solutions which are in equilibrium with the liquid solution at the temperature of the point C. These two solid solutions represent, in the one

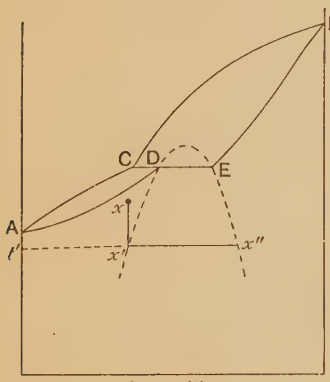


FIG. 51.

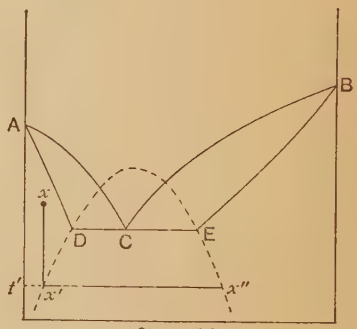


FIG. 52.

case a saturated solution of B in A (point D), and the other a saturated solution of A in B (point E). Just as we saw that the mutual solubility of two liquids varies with the temperature, so also in the case of two solids; as the temperature alters, the mutual solubility of the two solid components will change. This alteration is indicated diagrammatically in Figs. 51 and 52 by the dotted curve similar to the solubility curves for two mutually soluble liquids (p. 91).[1]

Suppose, now, that a solid solution of the composition x is cooled down, it will remain unchanged until, when the temperature has

[1] It should, perhaps, be pointed out that the two branches of the dotted curve below the temperature of the line DE represent stable systems. The rounded curve lying above DE represents no realisable system, since it lies above the melting-point of the solid solution. It has been put in merely to indicate more clearly the analogy between the mutual solubility curve for two liquids and that for two solids. A lower critical solution temperature, it may be added, has been realised in the case of solid solutions of ammonium chloride and manganous chloride dihydrate (Clendinnen and Rivett, *J. Chem. Soc.*, 1923, **123**, 1344).

fallen to t', the homogeneous solid solution breaks up into a conglomerate of two solid solutions the composition of which is represented by x' and x'' respectively. From this, then, it can be seen that in the case of substances which form two solid solutions, the solid solutions which are deposited from the liquid fused mass need not remain unchanged in the solid state, but may at some lower temperature lose their homogeneity. This fact is of considerable importance for the formation of alloys.[1]

A good example of this will soon be met with in the case of the iron and carbon alloys. The alloys of copper and tin also furnish examples of the great changes which may take place in the alloy between the temperature at which it separates out from the fused mass and the ordinary temperature. Thus, for example, one of the alloys of copper and tin which separates out from the liquid as a solid solution breaks up, on cooling, into the compound Cu_3Sn and liquid :[2] a striking example of a solid substance partially liquefying on being cooled.

II. The Components are not Completely Miscible in the Liquid State.

When one passes to the consideration of the equilibrium relations which exist in the case of two components which are not completely miscible in the liquid state, the additional complexity is introduced that at a certain value of the temperature and composition two liquid phases are formed. Since, at this point, there now coexist four phases, solid, two liquid phases, and vapour, the system is invariant.[3] Not only the temperature, therefore, but also the composition of the two liquid phases must have definite values. If the solid phase is allowed to be absent, then the system becomes univariant, and the composition of the two liquid phases will alter with the temperature. Into the ordinary equilibrium diagram, such as is represented in Figs. 33 and 37 (pp. 103 and 109), there will be introduced a curve for the relation between the temperature and the composition of the two liquid phases.

To illustrate the behaviour of such a system, we may consider the equilibrium diagram for the system water—succinic nitrile, which was fully studied by Schreinemakers.[4]

If to the system ice—water at 0° succinic nitrile is added, the temperature will fall ; and continued addition of the nitrile will lead at last to the eutectic point b (Fig. 53), at which solid nitrile, ice, solution, and vapour can coexist. The temperature of the eutectic

[1] See Roberts-Austen and Stansfield, *Rapports du congrès international de physique*, 1900, I., 363. See also Desch, *Metallography* (Longmans).

[2] Heycock and Neville, *Proc. Roy. Soc.*, 1903, **71**, 409. For the partial liquefaction of solid solutions on cooling, see also A. C. de Kock (*Z. physikal. Chem.*, 1904, **48**, 129).

[3] The system will still be invariant if the vapour phase be neglected but the pressure kept constant.

[4] *Z. physikal. Chem.*, 1897, **23**, 418.

point is — 1·2°, and the composition of the solution is 1·29 mol. of nitrile in 100 mol. of solution. From *a* to *b* the solid phase in contact with the solution is ice. If the temperature be now raised so as to cause the disappearance of the ice, and the addition of nitrile be continued, the concentration of the nitrile in the solution will increase as represented by the curve *bc*. The solid phase in equilibrium with the solutions represented by the curve *bc* is the nitrile. At the point *c* (18·5°), when the concentration of the nitrile in the solution has increased to 2·5 molecules per cent., the nitrile melts and two liquid phases are formed;[1] the concentration of the nitrile in these two phases is given by the points *c* and *c'*. As there are now four phases present, viz. solid nitrile, solution of fused nitrile in water, solution of water in fused nitrile, and vapour, the system is *invariant*. Since at this point the concentration, temperature, and pressure are completely defined, addition or withdrawal of heat can only cause a change in the relative amounts of the phases, *but no variation of the concentrations* of the respective phases. As a matter of fact, continued addition of nitrile and addition of heat will cause an increase in the amount of the liquid phase containing excess of nitrile (*i.e.* the solution of water in fused nitrile), whereas the other liquid phase, the solution of fused nitrile in water, will gradually disappear. When it has completely disappeared, the system will be represented by the point *c'*, where the molecular concentration of nitrile is now 75 per cent., and it again becomes univariant, the three phases being solid nitrile, liquid phase containing excess of nitrile, and vapour. As the amount of the water is diminished the temperature of equilibrium rises, until at 54° the melting-point of the pure nitrile is reached.

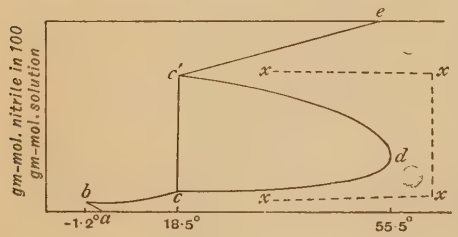


FIG. 53.

Return now to the point *c*. At this point there exists the invariant system solid nitrile, two liquid phases, vapour. If heat be added, the solid nitrile will disappear, and there will be left the univariant system consisting of two liquid phases and vapour.[2] Such a system will exhibit relationships similar to those already studied in the previous chapter. As the temperature rises, the mutual solubility of the two fused components becomes greater, until at *d* (55·5°) the critical solution temperature is reached, and the fused components become miscible in all proportions.

At all temperatures and concentrations lying to the right of the

[1] We have here the phenomenon of *melting under the solvent*. The phenomenon is also well seen in the case of paratoluidine which, when heated with water, melts at 44·2° and forms two liquid layers (Walker, *Z. physikal. Chem.*, 1890, **5**, 193).

[2] Provided the solid nitrile is not present in too great excess.

curve *abcdc'e* there can be only one liquid phase. At all temperatures between 18·5° and 55·5°, mixtures having a total composition represented by a point within the area *cdc'* will separate into two liquid phases.

From the figure it will be easy to see what will be the result of bringing together succinic nitrile and water at different temperatures and in different amounts. Since *b* is the lowest temperature at which liquid can exist in stable equilibrium with solid, ice and succinic nitrile can be mixed in any proportions at temperatures below *b* without undergoing change. Between *b* and *c* succinic nitrile will be dissolved until the concentration reaches the value on the curve *bc*, corresponding to the given temperature. On adding the nitrile to water at temperatures between *c* and *d*, it will dissolve until a concentration lying on the curve *cd* is attained; at this point two liquid phases will be formed, and further addition of nitrile will cause the one liquid phase (that containing excess of nitrile) to increase, while the other liquid phase will decrease, until it finally disappears and there is only one liquid phase left, that containing excess of nitrile. This can dissolve further quantities of the nitrile, and the concentration will increase until the curve *c'e* is reached, when the concentration will remain unchanged, and addition of solid will merely increase the amount of the solid phase.

If a solution represented by any point in the field lying below the curve *bcd* is heated to a temperature above *d*, the critical solution temperature, then the concentration of the nitrile can be increased to any desired amount without at any time two liquid phases making their appearance; the system can then be cooled down to a temperature represented by any point between the curves *dc'e*. In this way it is possible to pass continuously from a solution containing excess of one component to solutions containing excess of the other, as represented by the dotted line *xxxx*. At no point is there formation of two liquid phases.

Suspended Transformation.—Just as suspended transformation is rarely met with in the passage from the solid to the liquid state, so also it is found that in the case of the melting of substances under the solvent suspended fusion does not occur, but that when the temperature of the invariant point is reached at which, therefore, the formation of two liquid layers is possible, these two liquid layers, as a matter of fact, make their appearance. Suspended transformation can, however, take place from the side of the liquid phase, just as water or other liquid can be cooled below the normal freezing-point without solidification occurring. The question, therefore, arises as to the position of the equilibrium curve for the metastable, supercooled liquid phase.

The answer to this question can at once be given when we reflect that at temperatures at which the two liquid phases are metastable, the stable system, solid + liquid, must be capable of being formed from the metastable by separation of the solid phase. If, however,

separation of the solid phase takes place, the residuary liquid, which is in equilibrium with the solid phase, must contain a lower proportion of the crystallising component than does the metastable liquid. This was first proved experimentally by Alexejeff [1] in the case of benzoic acid and water, the equilibrium (solubility) curves for which are given in Fig. 54. As can be seen from the figure, the prolongation of the curve for liquid—liquid, which represents the solubility of the supercooled liquid benzoic acid, lies above that for the solubility of the solid benzoic acid in water; the solution saturated with respect to the

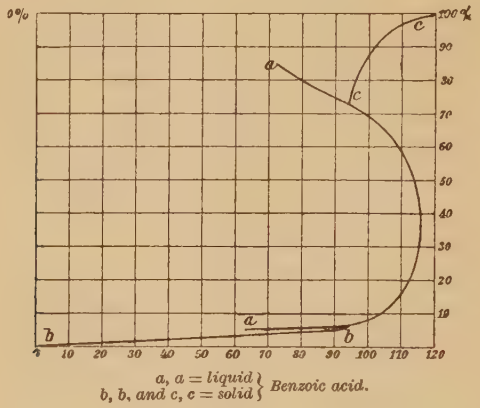


FIG. 54.

supercooled liquid is therefore supersaturated with respect to the solid form. A similar behaviour has been found in the case of other substances.[2]

[1] *Annalen d. Physik*, 1886, **28**, 328.

[2] Walker, *Z. physikal. Chem.*, 1890, **5**, 193; Schreinemakers, *ibid.*, 1897, **23**, 417; Roozeboom, *Rec. trav. chim. Pays-Bas*, 1889, **8**, 257; Bruner, *Z. physikal. Chem.*, 1897, **23**, 542. An interesting case of a liquid exhibiting a minimum solubility curve in a metastable region has been found in the case of dimethoxyacetphenetidide hydrate and water (Bogert and Ehrlich, *J. Amer. Chem. Soc.*, 1919, **41**, 741.

CHAPTER IX.

APPLICATION OF FREEZING-POINT CURVES TO THE STUDY OF SYSTEMS OF TWO COMPONENTS.

In this and the following chapters it is proposed to discuss the application of the principles of the Phase Rule, as developed in the preceding pages, to a number of systems of two components, so as to show more fully how the Phase Rule has been applied to the elucidation of certain problems connected with the equilibria between two components and how it has been employed for the interpretation of the data obtained by experiment. It is hoped that the practical value of the Phase Rule may thereby become more apparent, and its application to other cases be rendered easier.

(*a*) *Optically Active Substances.*

The question as to whether a resolvable inactive body is a mixture of the two oppositely active constituents (a *dl*-mixture), or a racemic compound, is one which has given rise to considerable discussion; and several investigators have endeavoured to establish general rules by which the question could be decided. In the case of inactive liquids it is a matter of great difficulty to arrive at a certain conclusion as to whether one is dealing with a mixture or a compound, for in this case the usual physical methods give but a dubious answer; and although the existence of a racemate in the liquid state (in the case of coniine) has been asserted,[1] many chemists incline to the belief that such a thing is improbable.

Even in the case of crystalline substances, where the differences between the various forms are greater, it is not always easy to discriminate between the *dl*-mixture and the racemic compound. The occurrence of hemihedral faces was considered by Pasteur to be a sufficient criterion for an optically active substance. It has, however, been found that hemihedry in crystals, although a frequent accompaniment of optical activity, is by no means a necessary or constant expression of this property. Other rules, also, which were given, although in some cases reliable, were in other cases insufficient; and all were in so far unsatisfactory that they lacked a theoretical basis.

With the help of the Phase Rule, however, it is possible from a

[1] Ladenburg, *Ber.*, 1895, **28**, 163, 1991; Mitchell and Smith, *J. Chem. Soc.*, 1913, **103**, 489; Smith, *ibid.*, 1914, **105**, 1703.

study of the solubility or fusion curves of the optically active and inactive substances, to decide the nature of the inactive substance, at least under certain conditions. On account of the interest and importance which these compounds possess, a brief description of the application of the Phase Rule to the study of such substances will be given here;[1] the two optical antipodes being regarded as the two components.

In the present chapter we shall consider only the fusion curves, the solubility curves being discussed in the next section on three-component systems. The rules which are hereby obtained have reference only to the nature of the inactive substance in the neighbourhood of the melting-points.

1. *The inactive substance is a* dl-*mixture.*

In this case the fusion curves will have the simple form shown in Fig. 33. A and B in Fig. 33 would represent the melting-points of the two optical isomerides (the temperature, however, being the same

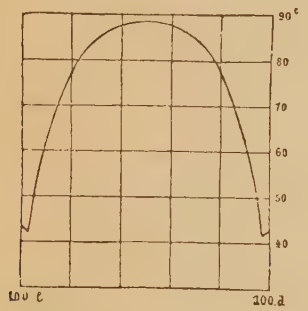


FIG. 55.

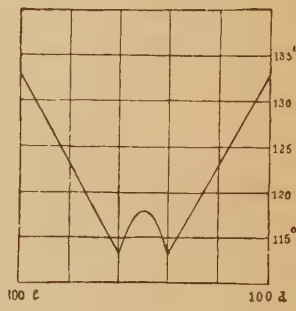


FIG. 56.

for both isomerides), and C the eutectic point at which the inactive mixture (conglomerate), consisting of equal amounts of *d*- and *l*- form, melts. Owing to the similar effect of the one form on the freezing-point of the other, the figure is symmetrical. The only known example of this type of system is found in the case of *d*- and *l*-pinene.[2] The melting-point of the active isomerides is — 63° to — 64°, and the eutectic temperature is about — 120°.

2. *The two components form a racemic compound.*

In this case there will be three melting-point curves as in Fig. 37, type I. In this case also the figure must be symmetrical.

Examples.—As examples of this there may be taken dimethyl tartrate and mandelic acid, the freezing-point curves of which are given in Figs. 55 and 56.[3] As can be seen, the curve for the racemic

[1] Roozeboom, *Z. physikal. Chem.*, 1899, **28**, 494; Adriani, *ibid.*, 1900, **33**, 453. See also van Laar, *ibid.*, 1908, **64**, 257; Tammann, *ibid.*, 1914, **87**, 357.

[2] Ross and Somerville, *J. Chem. Soc.*, 1926, p. 2770.

[3] Adriani, *Z. physikal. Chem.*, 1900, **33**, 453.

tartrate occupies a large part of the diagram, while that for racemic mandelic acid is much smaller. In the case of dimethyldiacetyl tartrate, this middle portion is still less.

Active dimethyl tartrate melts at 43·3°; racemic dimethyl tartrate at 89·4°. Active mandelic acid melts at 132·8°; the racemic acid at 118·0°. In the one case, therefore, the racemic compound has a higher, in the other a lower, melting-point than the active forms.

Camphoric acid and *o*-methylhydrogen camphorate also yield curves indicating the formation of a crystalline racemate with a congruent melting-point.[1]

In the case of partially racemic compounds (*i.e.* the compound of a racemate with an optically active substance) the type of curve will

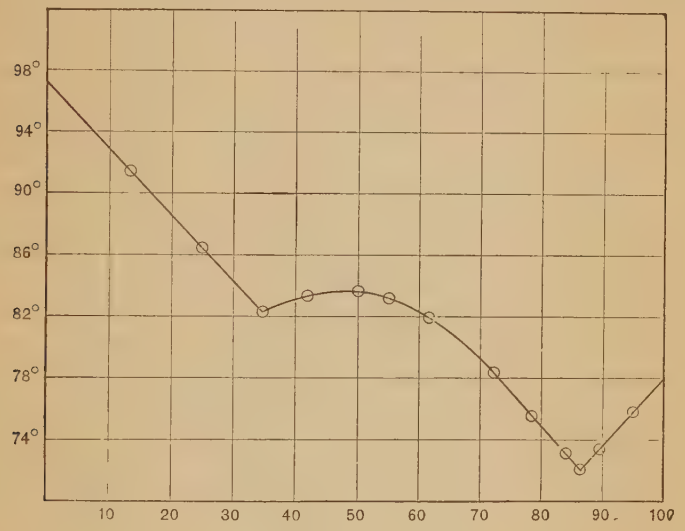


FIG. 57.

be the same, but the figure will no longer be symmetrical. Such a curve has been found in the case of the *l*-menthyl esters of *d*- and *l*-mandelic acid (Fig. 57).[2] The freezing-point of *l*-menthyl *d*-mandelate is 97·2°, of *l*-menthyl *l*-mandelate 77·6°, and of *l*-menthyl *r*-mandelate 83·7°.

It will be observed that the summit of the curve for the partially racemic mandelate is fairly flat, indicating, as we have already seen (p. 109), that the compound is dissociated to a considerable extent in the liquid state. Employing the method given on page 110, the degree of dissociation was calculated to be about 40-50 per cent. By a

[1] Ross and Somerville, *J. Chem. Soc.*, 1926, p. 2770.

[2] A. Findlay and Miss E. Hickmans, *J. Chem. Soc.*, 1907, **91**, 905. See also Dutilh, *Verhandelingen K. Akad. Wetensch. Amsterdam*, 1912, **11**, Sect. I.

similar method, Ross and Somerville calculated the degree of dissociation of racemic camphoric acid to be about 12 per cent., and that of racemic *o*-methylhydrogen camphorate to be about 18 per cent. In the case of racemic benzoyltetrahydroquinaldine the crown of the curve is relatively sharp,[1] and a comparatively small degree of dissociation may therefore be assumed.

From the investigation, therefore, of the compounds mentioned the conclusion may certainly be drawn that undissociated racemic molecules exist in the liquid state.

3. *The inactive substance is a pseudo-racemic mixed crystal* (*solid solution*).

In cases where the active components can form mixed crystals or solid solutions, the freezing-point curve will exhibit one of the forms given in Figs. 43 and 48. The inactive mixed crystal containing 50 per cent. of the dextro and lævo compound, is known as a pseudo-racemic mixed crystal.[2] So far, only curves of the types I. and II. have been obtained.

Examples.—The two active camphor oximes are of interest from the fact that they form a continuous series of solid solutions, *all of which have the same melting-point.* The curve which is obtained in this case is, therefore, a straight line joining the melting-points of the pure active components; the melting-point of the active isomerides and of the whole series of solid solutions being 118·8°. Curves of this type are also given by borneol, camphor, camphoric anhydride, bornyl hydrogen phthalate and camphene.[3]

In the case of the carvoximes solid solutions are also formed, but the equilibrium curve in this case exhibits a maximum (Fig. 58). At this maximum point the composition of the solid and of the liquid solution is the same. Since the curve must be symmetrical, this maximum point must occur in the case of the solution containing 50 per cent. of each component, which will therefore be inactive. Further, this inactive solid solution will melt and solidify at the same temperature, and behave, therefore, like a chemical compound (p. 121). The melting-point of the active compounds is 72°; that of the inactive pseudo-racemic mixed crystal is 91·4°.

FIG. 58.

Transformations.—As has already been remarked, the conclusions which can be drawn from the fusion curves regarding the nature of the inactive substances formed, hold only for temperatures in the neigh-

[1] Adriani, *Z. physikal. Chem.*, 1900, **33**, 453.
[2] Kipping and Pope, *J. Chem. Soc.*, 1897, **71**, 993.
[3] Ross and Somerville, *ibid.*, 1926, p. 2770.

bourhood of the melting-points. At temperatures below the melting-point transformation may occur; *e.g.* a racemate may break up into a *dl*-mixture, or a pseudo-racemic mixed crystal may form a racemic compound. We shall at a later point meet with examples of a racemic compound changing into a *dl*-mixture at a definite transition point; and the pseudo-racemic mixed crystal of camphoroxime is an example of the second transformation. Although at temperatures in the neighbourhood of the melting-point the two active camphoroximes form only mixed crystals but no compound,[1] a racemic compound is formed at temperatures below 103°. At this temperature the inactive pseudo-racemic mixed crystal changes into a racemic compound; and in the case of the other solid solutions transformation to racemate and (excess of) active component also occurs, although at a lower temperature than in the case of the inactive solid solution. Although this behaviour is one of considerable importance, this brief reference to it must suffice here.[2]

(*b*) *Alloys.*

One of the most important classes of substances in the study of which the Phase Rule has been of very considerable importance, is that formed by the mixtures or compounds of metals with one another known as alloys. Although in the investigation of the nature of these bodies various methods are employed, one of the most important is the determination of the character of the freezing-point curve; for from the form of this valuable information can, as we have already learned, be obtained regarding the nature of the solid substances which separate out from the molten mixture.

Although it is impossible here to discuss fully the experimental results and the oftentimes very complicated relationships which the study of the alloys has brought to light, a brief reference to these bodies will be advisable on account both of the scientific interest and of the industrial importance attaching to them.[3]

[1] That is, no compound capable of existing as solid phase in equilibrium with liquid mixtures. A racemic compound may be formed which yields solid solutions with the optically active isomerides.

[2] See Roozeboom, *Z. physikal. Chem.*, 1899, **28**, 512; Adriani, *ibid.*, 1900, **33**, 473; 1901, **36**, 168.

[3] In this connection reference should be made more especially to the paper by Roberts-Austen and Stansfield, "Sur la constitution des alliages métalliques," in the *Rapports du congrès international de physique*, 1900, I., 363; J. A. Mathews, *J. Franklin Inst.*, 1902; Gautier, *Compt. rend.*, 1896, **123**, 109; Roberts-Austen, "Reports of the Alloys Research Committee," in *J. Inst. Mechan. Engineers*, from 1891 to 1904; and the papers by Heycock and Neville, published in the *J. Chem. Soc.*, and the *Trans. Roy. Soc.* since 1897; also Neville, *Reports of the British Association*, 1900, p. 131. Reference must also be made to the important metallographic investigations by Tammann and his pupils, and of Kurnakov (*Z. anorgan. Chem.*, vol. **40** and onwards), and also to those of Shepherd, *J. Physical Chem.*, **8**. A bibliography of the alloys is given in *Z. anorgan. Chem.*, 1903, **35**, 249, and by Estis, *Met. and Chem. Eng.*, 1917, **16**, 273. See also the volume in this series on *Metallography*, and the monograph on *Inter-metallic Compounds*, by C. H. Desch; Mlodziejowski, *Z. physikal. Chem.*, 1925, **117**, 361.

We have already seen that there are three chief types of freezing-point curves in systems of two components, viz. those obtained when (1) the pure components crystallise out from the molten mass; (2) the components form one or more compounds; (3) the components form solid solutions. In the case of the metals, representatives of these three classes are also found. A mathematical analysis of the freezing-point curves on the basis of the formulæ for ideal solutions (p. 104) has been carried out by Andrews and Johnston.[1]

1. *The components separate out in the pure state.*

In this case the freezing-point curve is of the simple type (Fig. 33). Such curves have been obtained in the case of a number of pairs of metals, *e.g.* zinc—cadmium, zinc—aluminium, copper—silver (Heycock and Neville), tin—zinc, bismuth—lead (Gautier), and in other cases. From molten mixtures represented by one branch of the freezing-point curve one of the metals will be deposited; while from mixtures represented by the other branch, the other metal will separate out. At the eutectic point the molten mass will solidify to a *heterogeneous mixture* of the two metals, forming what is known as the *eutectic alloy*.[2] Such an alloy, therefore, will melt at a definite temperature lower than the melting-point of either of the pure metals.

In the following table are given the temperature and the composition of the liquid at the eutectic point, for three pairs of metals:—

	Temperature.	Composition of liquid.
Zinc—cadmium . .	264·5°	73·5 atoms per cent. of cadmium.
Zinc—aluminium . .	380·5°	11 ,, ,, aluminium.
Copper—silver . .	778°	40 ,, ,, copper.

The melting-points of the pure metals are: zinc, 419°; cadmium, 322°; silver, 960°; copper, 1081°; aluminium, 650°.

2. *The two metals can form one or more compounds.*

In this case there will be obtained not only the freezing-point curves of the pure metals, but each compound formed will have its own freezing-point curve. If the compound have a congruent melting-point, the equilibrium curve will exhibit a point of maximum temperature, and will end, on either side, in an eutectic point. The simplest curve of this type will be obtained when only one compound is formed, as is the case with mercury and thalium.[3] This curve is represented in Fig. 59, where the summit of the intermediate curve corresponds with a composition $TlHg_2$. Similar curves are also given by nickel and tin, by aluminium and silver, and by other metals, the formation of

[1] *Inst. Met.*, 1924, **32**, 385.

[2] As is to be expected from the manner of its formation, the eutectic alloy is shown, by microscopic examination, to have a characteristic, fine texture.

[3] Kurnakov and Puschin, *Z. anorgan. Chem.*, 1902, **30**, 104.

definite compounds between these pairs of metals being thereby indicated.[1]

A curve belonging to the same type, but more complicated, is obtained with gold and aluminium ; [2] in this case, several compounds are formed, some of which have a congruent melting-point, while others have an incongruent melting-point. The chief compound is $AuAl_2$, which has practically the same melting-point as pure gold.

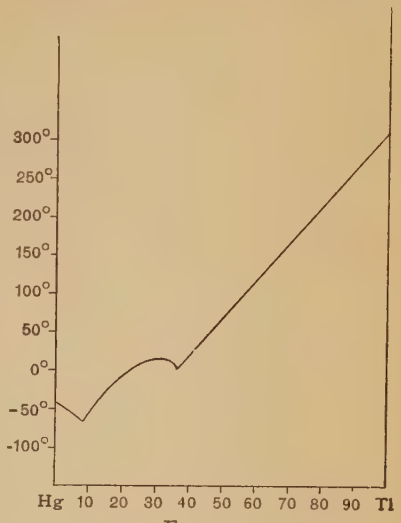


FIG. 59.

3. *The two metals form solid solutions.*

The simplest case in which the metals crystallise out together in solid solution is found in silver and gold.[3] The freezing-point curve in this case is an almost straight line joining the freezing-points of the pure metals (*cf.* curve I., Fig. 43, p. 119). These two metals, therefore, can form an unbroken series of solid solutions.[4]

In some cases, however, the two metals do not form an unbroken series of solid solutions. In the case of zinc and silver,[5] for example the addition of silver *raises* the freezing-point of the mixture, until a transition point is reached. This corresponds with curve I., Fig. 48. Silver and copper, and gold and copper, on the other hand, do not form unbroken series of mixed crystals, but the freezing-point curve exhibits an eutectic point, as in curve II., Fig. 48. In these cases, liquid mixtures having the composition of the point C deposit, on freezing, a mixture of *two solid solutions*, the composition of which is represented diagrammatically by the points D and E.

Not only may there be these three different types of curves, but there may also be combinations of them. Thus the two metals may not only form compounds, but one of the metals may not separate out in the pure state at all, but form solid solutions. In this case the

[1] Gautier, *Bull. Soc. d'Encouragement*, 1896 [5], **1**, 1312.

[2] Heycock and Neville, *Phil. Trans.*, 1900, **194**. 201.

[3] Gautier, *loc. cit.* See also Roberts-Austen and Rose, *Proc. Roy. Soc.*, 1903, **71**, 161.

[4] Since diffusion takes place relatively slowly in a solid solution, the solid which is deposited from a molten mixture will not be uniform. By "annealing" such an alloy, that is, by heating for some time to a temperature below the melting-point, diffusion takes place and a homogeneous solid solution is produced.

[5] Heycock and Neville, *J. Chem. Soc.*, 1897, **71**, 414.

freezing-point may rise (as in the case of silver and zinc), and one of the eutectic points will be absent.

Iron-Carbon Alloys.—Of all the different binary alloys, probably the most important are those formed by iron and carbon: alloys consisting not of two metals, but of a metal and a non-metal. On account of the importance of these alloys, an attempt will be made to describe in brief some of the most important relationships met with.

Before proceeding to discuss the application of the Phase Rule to the study of the iron-carbon alloys, however, the main facts with which we have to deal may be stated very briefly.

Iron is capable of existing in three distinct solid phases, known as α-, γ- and δ-ferrite respectively. α-ferrite and δ-ferrite have been shown by X-ray examination [1] to have body-centred cubic lattices, varying only in dimensions with temperature,[2] while γ-ferrite has a face-centred cubic lattice. δ-ferrite [3] is the stable form of iron above 1400°, and undergoes change to γ-ferrite below this temperature. Between 1400° and 900° γ-ferrite is stable, while below 900° α-ferrite becomes the stable form.

With regard to β-ferrite, it has been fully established that the change formerly spoken of as the A_2 or α—β change, does not represent a phase transformation at all, but a magnetic transformation which, unlike a polymorphic or phase transformation, does not take place at a definite temperature, but is a progressive change, the velocity of which is a function of the temperature. β-ferrite, therefore, does not exist as a distinct phase.

Owing to the fact that the phase changes $\delta \rightarrow \gamma$ and $\gamma \rightarrow \alpha$ are accompanied by evolution of heat, the cooling curve of iron, below its melting-point, shows an arrest at the temperatures at which the phase changes occur. The arrest on the cooling curve corresponding with the change $\delta \rightarrow \gamma$ is referred to as Ar_4 (A = arrêt = arrest; r = refroidissement = cooling); and the arrest at the temperature of change $\gamma \rightarrow \alpha$ is known as Ar_3. Similarly, the arrests on the heating curve (*chauffage*) are known as Ac_4 and Ac_3. For Ar_4 and Ac_4, the values 1400° and 1410° respectively have been found; while Ar_3 and Ac_3 have the values 894° and 904°.

A short description may now be given of the application of the Phase Rule to the two-component system iron—carbon; and of the diagram showing how the different systems are related, and with the help of which the behaviour of the different mixtures under given conditions can be predicted.

[1] Bain, *Chem. and Met. Eng.*, 1921, **25**, 663; Westgren, *J. Iron and Steel Inst.*, 1921, **103**, 303; Westgren and Phragmén, *ibid.*, 1922, **105**, 241; *Z. physikal. Chem.*, 1922, **102**, 1.

[2] It has been shown by Honda (*Sci. Rep. Tôhoku Imp. Univ.*, 1925, **13**, 363) that δ-ferrite lies on the same curve of properties as α-ferrite, and that it is therefore identical with it as a phase. See also Sato, *Phil. Mag.*, 1926 [7], **1**, 996; *Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 513.

[3] Osmond, *J. Iron and Steel Inst.*, 1890, I. 102; Ruer and Klesper, *Ferrum*, 1914, **11**, 257; Ruer and Goerens, *ibid.*, 1916, **14**, 161.

The most important equilibrium relations met with in the case of the iron-carbon alloys are represented graphically in Figs. 60 and 61.

In Fig. 60 are represented the equilibrium relations for δ-ferrite, determined by Ruer and Goerens.[1] In this diagram, D represents the transition point for δ- and γ-ferrite (1400° C.). This transition point is greatly raised by addition of small amounts of carbon, as indicated by the curve DE, until at the point E, when the amount of carbon is about 0·1 per cent., the transition point lies at 1487°, and the transition curve ends in the curve of complete solidification, AE.[2] This

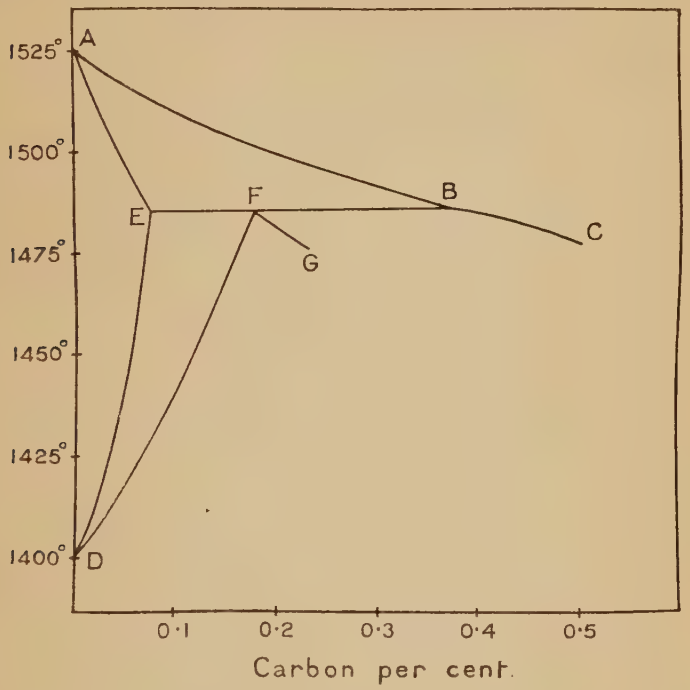


FIG. 60.

curve, AE, gives the composition of the solid solutions of δ-ferrite and carbon in equilibrium with the molten mixtures AB. At the temperature of the horizontal EFB (1487°), the molten mixture is in equilibrium with the two solid phases, δ-ferrite solid solutions (E) and γ-ferrite solid solutions (F). At B, the melt contains about 0·4 per cent. of carbon. The position of F (composition of the γ-ferrite solid solutions) is not known with accuracy.

From melts containing less than 0·1 per cent. of carbon (E), δ-solid

[1] *Ferrum*, 1916, **14**, 161.

[2] The melting-point of pure iron (δ-ferrite) is shown here at about 1525° C. The melting-point found by Carpenter (see later) is 1505°.

solutions first separate out, and these then, on cooling, undergo transformation (along ED) into γ-solid solutions. From melts containing between 0·1 and 0·4 per cent. of carbon, δ-ferrite solid solutions first separate, and these on cooling to 1487°, change, through reaction with the melt, into δ- and γ-solid solutions (E and F). It is here assumed that equilibrium is constantly being established (see p. 119). From melts containing more than 0·4 per cent. of carbon, γ-solid solutions only separate out (curve FG, Fig. 60).

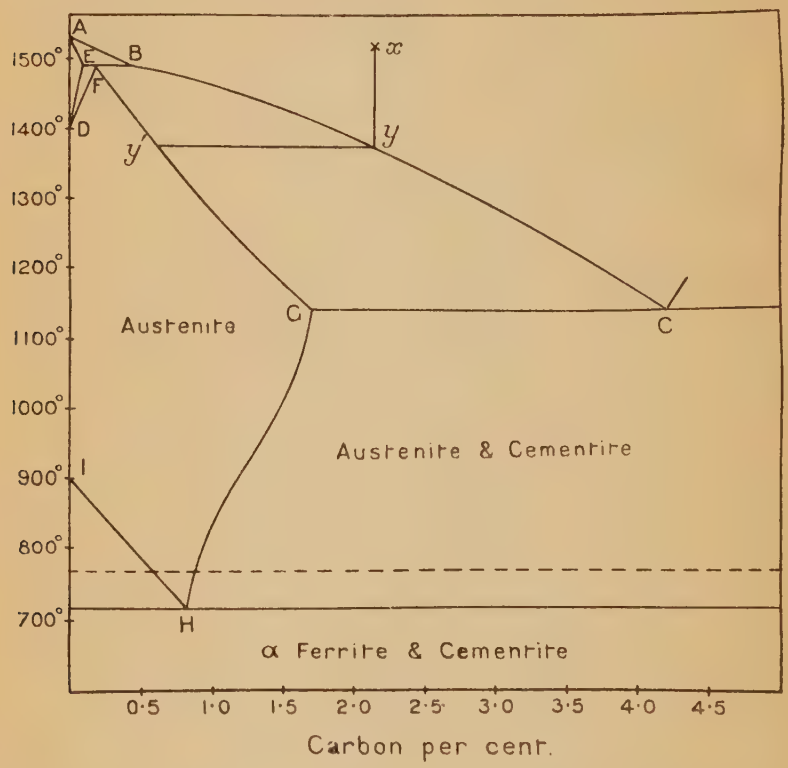


FIG. 61.

The area ADE represents the region of stability of δ-ferrite; the area DEF the region in which δ-ferrite solid solutions and γ-ferrite solid solutions are in equilibrium; and the area AEB is the area for δ-solid solutions and molten mixtures.

In Fig. 61 is given the complete equilibrium diagram.[1] The curves

[1] The diagram given here is due to Honda, *J. Iron and Steel Inst.*, 1922, **105**, 381, and to Ruer and Goerens, *Ferrum*, 1916, **14**, 161. See also Ruer, *Z. anorgan. Chem.*, 1920, **113**, 98; 1921, **117**, 249; Kaya, *Sci. Rep. Tôhoku Imp. Univ.*, 1925, **14**, 529. References to older diagrams, now known to be inaccurate, will be found in the earlier editions of this work.

AB and BC are the freezing-point curves for solutions of carbon in iron (δ-ferrite and γ-ferrite respectively), starting from the melting-point of pure iron (δ-ferrite).[1] C is a eutectic point. Suppose that we start with a molten mixture of iron and carbon, represented by the point x, containing more than 0·4 per cent. of carbon.[2] On allowing the temperature to fall, a point, y, will be reached at which solid begins to separate out. This solid phase, however, is not pure iron, but a solid solution of carbon in γ-ferrite, known as austenite, having a composition represented by y' (cf. p. 119). As the temperature continues to fall, the composition of the liquid phase changes in the direction yC, while the composition of the solid phase which separates out changes in the direction y'G; and, finally, when the composition of the molten mass is that of the point C (4·3 per cent. of carbon), the whole mass solidifies to a heterogeneous mixture of saturated austenite (saturated solution of carbon in γ-ferrite) and cementite, Fe_3C, represented respectively by G and by a point on an extension of the line GC corresponding with 6·7 per cent. of carbon. The saturated austenite (point G) contains 1·8 per cent. of carbon. The temperature of the eutectic point is 1125° C.[3]

Even below the solidification point, changes can take place. As the saturated austenite is cooled below 1125°, separation of cementite takes place along GH, the percentage of carbon in the saturated austenite diminishing with fall of temperature, until at about 700°,[4] the limit of saturation is reached at 0·89 per cent. of carbon (point H). Below this eutectoid point H, separation into α-ferrite and cementite takes place (A1 transformation). This eutectoid mixture is known as *pearlite*.

From the above discussion it follows that if we start with a molten mixture of iron and carbon, the composition of which is represented by any point between G and C (1·8 to 4·3 per cent. of carbon), we shall obtain, on cooling the mass, first of all solid solutions, the composition of which will be represented by points on the curve FG; then, after the mass has completely solidified at 1125°, further cooling will lead to a separation of cementite and a change in the composition of the austenite (from 1·8 to 0·89 per cent. of carbon), until, at temperatures below about 700° the austenite becomes heterogeneous and forms pearlite and cementite.

It has already been mentioned that γ-ferrite undergoes transformation into α-ferrite at about 900°. This transition point is represented

[1] The melting-point of iron has been found by Carpenter (*J. Iron and Steel Inst.*, 1908, **69**, 290) to be 1505° C.

[2] The behaviour which is found when the molten mixtures contain less than 0·4 per cent. of carbon has already been discussed.

[3] According to Ruer and Goerens (*Ferrum*, 1916, **14**, 161), the temperature is 1145°.

[4] See Ruer and Goerens, *Ferrum*, 1916, **14**, 161; Saldaou and Goerens, *J. Russ. Met. Soc.*, 1914, **1**, 789; *Rev. de Métal.*, 1917, **14**, E., 65; Honda, *J. Iron and Steel. Inst.*, 1922, **105**, 381.

in Fig. 61 by the point I. Since γ-ferrite dissolves carbon, the transition point depends on the amount of carbon present, and falls with increase in the percentage of carbon as shown by the curve IH. If an austenite containing less carbon than is represented by the point H is cooled down slowly from a temperature of, say, 900°, then when the temperature has fallen to that represented by a point on the curve IH, α-ferrite will separate out; and, as the temperature falls, the composition of the solid solution will alter as shown by the curve IH. When the temperature reaches that represented by the point H, the solid solution will break up into pearlite (α-ferrite and cementite).

We see, therefore, that when austenite is allowed to cool *slowly*, it yields a heterogeneous mixture either of ferrite and pearlite (when the original mixture contained up to 0·8 per cent. of carbon), or pearlite and cementite (when the original mixture contained between 0·8 and 1·8 per cent. of carbon). These heterogeneous mixtures constitute soft steels, or, when the carbon content is low, wrought iron.

The case, however, is different if the solid solution of carbon in iron is *rapidly* cooled (quenched) from a temperature above the curve IHG to a temperature below this curve. In this case, although the rapid cooling does not completely prevent the resolution of the solid solution, austenite, into ferrite or cementite, the resolution is not so complete as when cooling takes place slowly; and in this way hard steel is obtained. By varying the rapidity of cooling, as is done in the tempering of steel, varying degrees of resolution of the austenite are produced, and so varying degrees of hardness obtained.[1]

The horizontal dotted line shown in Fig. 61 represents what is known as the A2 transformation. This, as has already been mentioned, was formerly thought to be a phase transformation of α- into β-ferrite, but it is now known to represent merely a magnetic transformation, which takes place progressively, beginning at a low temperature and ending at about 790° C. This transformation differs from a phase transformation in the fact that it begins but does not progress to completion with time at temperatures below 790°. This is the temperature at which the A2 transformation begins on cooling and ends on heating, and it is independent of the carbon content, as shown by the horizontal, dotted line. This line was first detected by Carpenter and Keeling,[2] but has been more fully studied in recent times by Honda.[3]

(*c*) *Minerals.*

Important and interesting as is the application of the Phase Rule to the study of alloys, its application to the study of the conditions

[1] See Humphrey (*Chem. News*, 1914, **110**, 271) for the part played by the amorphous phase in the hardening of steels.

[2] *J. Iron and Steel Inst.*, 1904, **65**, 224.

[3] *Sci. Rep. Tôhoku Imp. Univ.*, 1915, **4**, 169; *J. Iron and Steel Inst.*, 1915, **91**, 199; **92**, 181; *Sci. Rep. Tôhoku Imp. Univ.*, 1917, **6**, 213; *J. Iron and Steel Inst.*, 1922, **105**, 381; *ibid.*, 1925, **112**, 345.

regulating the formation of minerals is no less so; and although we do not propose to consider different cases in detail here, attention must be drawn to certain points connected with this interesting subject.

In the first place, it will be evident from what has already been said, that the mineral which first crystallises out from a molten magma is not necessarily the one with the highest melting-point. The *composition* of the fused mass must be taken into account. When the system consists of two components which do not form a compound, one or other of these will separate out in a pure state, according as the composition of the molten mass lies on one or other side of the eutectic composition; and the separation of the one component will continue until the composition of the eutectic point is reached. Further cooling will then lead to the simultaneous separation of the two components.

If, however, the two components form a stable compound (*e.g.* orthoclase, from a fused mixture of silica and potassium aluminate), then the freezing-point curve will resemble that shown in Fig. 37, curve I.; *i.e.* there will be a middle curve possessing a dystectic point, and ending on either side at a eutectic point. This curve would represent the conditions under which orthoclase is in equilibrium with the molten magma. If the initial composition of the magma is represented by a point between the two eutectic points, orthoclase will separate first. The composition of the magma will thereby change, and the mass will finally solidify to a mixture of orthoclase and silica, or orthoclase and potassium aluminate, according to the initial composition.[1]

What has just been said holds, however, only for stable equilibria, and it must not be forgotten that complications can arise owing to suspended transformation (when, for example, the magma is rapidly cooled) and the production of metastable equilibria. These conditions occur very frequently in nature.

The study of the formation of minerals from the point of view of the Phase Rule is now attracting considerable attention,[2] and reference to some recent work in this department will be made later (p. 223).

[1] For a study of the binary system MgO—SiO_2, see Bowen and Andersen, *Amer. J. Sci.*, 1914 [4], **37**, 487. For the system Al_2O_3—SiO_2, see Bowen and Greig, *J. Amer. Cer. Soc.*, 1924, **7**, 238.

[2] In this connection, see Doelter, *Physikalisch-chemische Mineralogie* (Barth, 1901); Meyerhoffer, *Z. Krist.*, 1902, **36**, 593; Guthrie, *Phil. Mag.*, 1884 [5], **17**, 479; Le Chatelier, *Compt. rend.*, 1900, **130**, 85; and especially E. Baur, *Z. physikal. Chem.*, 1903, **42**, 567; J. H. L. Vogt, *Z. Elektrochem.*, 1903, **9**, 852, and *Die Silikatschmelzlösungen*, Parts I. and II. (Christiania, 1903, 1904). See also N. V. Kultascheff, *Z. anorgan. Chem.*, 1903, **35**, 187; Doelter, *Monatsh.*, 1906, **27**, 433; Day and Allen, *Z. physikal. Chem.*, 1905, **54**, 1; Day and Shepherd, *J. Amer. Chem. Soc.*, 1906, **28**, 1089; Reiter, *Jahrb. Min.*, 1906, *Beil.-Bd.*, **22**, 183; Lebedeff, *Z. anorgan. Chem.*, 1911, **70**, 301; Bowen, *ibid.*, 1913, **82**, 283; Deleano, *ibid.*, 1914, **84**, 401; Day, *Fortschr. d. Min. Kristall., Petrog.*, 1914, **4**, 115; Rastall, *Physico-chemical Geology* (Arnold).

CHAPTER X.

APPLICATION OF FREEZING-POINT CURVES TO THE STUDY OF SYSTEMS OF TWO COMPONENTS (*Continued*).

(*d*) *Dynamic Isomerides and Pseudo-binary Systems.*

In the systems hitherto discussed (except sulphur and phosphorus), the components behaved, or were regarded as behaving, as strictly unary substances; that is, the molecules of each component in all the phases in which it occurred were identical both physically and chemically. Each component formed only one molecular species, and the number of molecular species was, therefore, equal to the number of the components. The systems were purely unary (one-component) or purely binary (two-component).

But there are not a few systems in which the number of molecular species is greater than the number of components; that is, substances which have the same chemical composition (but which may be isomeric forms) may give rise to different molecular species, between which, in the liquid or vapour state, a condition of equilibrium can exist. This fact may alter very markedly the behaviour of a system. Although, therefore, a system may appear to be unary, so far as chemical composition is concerned, it may, as a matter of fact, behave in some respects as a binary system. It forms a pseudo-binary system. The behaviour of these systems, as we shall see, depends largely on the rate at which the internal equilibrium between the different molecular species in the liquid or vapour phase is established. In the present chapter some of the more important aspects of these pseudo-binary systems will be considered.

It has long been known that certain substances, *e.g.* acetoacetic ester, are capable when in solution or in the fused state of reacting as if they possessed two different constitutions; and in order to explain this behaviour the view was advanced (by Laar) that in such cases a hydrogen atom oscillated between two positions in the molecule, being at one time attached to oxygen, at another time to carbon, as represented by the formula

When the hydrogen is in one position, the substance will act as an hydroxy-compound; with hydrogen in the other position, as a ketone. Substances possessing this double function are called *tautomeric*.

Doubt, however, arose as to the validity of the above explanation, and this doubt was confirmed by the isolation of the two isomerides in the solid state, and also by the fact that the velocity of change of the one isomeride into the other could in some cases be quantitatively measured. These and other observations then led to the view, in harmony with the laws of chemical dynamics, that tautomeric substances in the dissolved or fused state represent a *mixture* of two isomeric forms, and that equilibrium is established not by *intra-* but by *inter*-molecular change, as expressed by the equation

$$CH_3 . CO . CH_2 . CO_2C_2H_5 \rightleftarrows CH_3 . C(OH) : CH . CO_2C_2H_5.$$

In the solid state, the one or other of the isomerides represents the stable form; but in the liquid state (solution or fusion) the stable condition is an equilibrium between the two forms.

A similar behaviour is also found in the case of other isomeric substances where the isomerism is due to difference of structure, *i.e.* structure isomerism

$$\left(\textit{e.g.}\text{ in the case of the oximes } \begin{matrix} C_6H_5 . C . H \\ \| \\ N . OH \end{matrix} \text{ and } \begin{matrix} C_6H_5 . C . H \\ \| \\ HO . N \end{matrix}\right),$$

or to difference in configuration, *i.e.* stereoisomerism (*e.g.* optically active substances), or to polymerism (*e.g.* acetaldehyde and paraldehyde). In all such cases, although the different solid forms correspond to a single definite constitution, in the liquid state a condition of equilibrium between the two modifications is established. As a general name for these different classes of substances, the term "dynamic isomerides" has been introduced; and the different kinds of isomerism are classed together under the title "dynamic isomerism." [1]

By reason of the importance of these phenomena in the study more especially of Organic Chemistry, a brief account of the equilibrium relations exhibited by systems composed of dynamic isomerides may be given here.[2]

In studying the fusion and solidification of those substances which exhibit the relationships of dynamic isomerism, it has to be borne in mind that the phenomena observed will vary somewhat according as the reversible transformation of the one form into the other takes place with measurable velocity at temperatures in the neighbourhood of the melting-points, or only at some higher temperature. If the transformation is relatively very rapid, the system will behave like a one-component system, but if the isomeric change is comparatively slow, the behaviour will be that of a two-component system.

Temperature-Concentration Diagram.—The relationships which

[1] Armstrong, *Watt's Dictionary of Chemistry* (Morley and Muir), III., p. 88. See also Lowry, *J. Chem. Soc.*, 1899, **75**, 211.

[2] See Bancroft, *J. Physical Chem.*, 1898, **2**, 143; Roozeboom, *Z. physikal. Chem.*, 1899, **28**, 288; *Die heterogenen Gleichgewichte*, Vol. II., Part 3 (Vieweg, 1918).

are met with here will be most readily understood with the help of Fig. 62. Suppose, in the first instance, that isomeric transformation does not take place with appreciable velocity at the temperature of the melting-point, then the freezing-point curve will have the simple form ACB; the formation of compounds being for the present excluded. This is the simplest type of curve, and gives the composition of the solutions in equilibrium with the one modification (α-modification) at different temperatures (curve AC); and of the solutions in equilibrium with the other modification (β-modification) at different temperatures (curve BC). C is the eutectic point at which the two solid isomerides can exist side by side in contact with the solution.

Now, suppose that isomeric transformation takes place with measurable velocity. If the pure α-modification is heated to a temperature t' above its melting-point, and the liquid maintained at that temperature until equilibrium has been established, a certain amount of the β-form will be present in the liquid, the composition of which will be represented by the point x'. The same condition of equilibrium will also be reached by starting with pure β. Similarly, if the temperature of the liquid is maintained at the temperature t'', equilibrium will be reached, we shall suppose, when the solution has the composition x''. The curve DE, therefore, which passes through all the different values of x corresponding to different values of t, will represent the change of equilibrium with the temperature. It will slope to the right (as in the figure) if the transformation of α into β is accompanied by absorption of heat; to the left if the transformation is accompanied by evolution of heat, in accordance with the theorem of Le Chatelier. If transformation occurs without heat effect, the equilibrium will be independent of the temperature, and the equilibrium curve DE will therefore be parallel to the temperature axis.

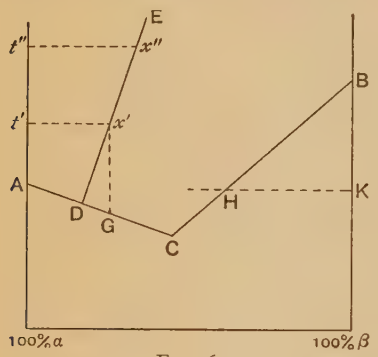


FIG. 62.

We must now find the meaning of the point D. Suppose the pure α- or pure β-form heated to the temperature t', and the temperature maintained constant until the liquid has the composition x' corresponding to the equilibrium at that temperature. If the temperature is now allowed to fall sufficiently slowly so that the condition of equilibrium is continually readjusted as the temperature changes, the composition of the solution will gradually alter as represented by the curve x'D. Since D is on the freezing-point curve of pure α, this form will be deposited on cooling; and since D is also on the equilibrium curve of the liquid, D is the only point at which solid can exist in stable equilibrium with the liquid phase. (The vapour phase may be

omitted from consideration, as we shall suppose the experiments carried out in open vessels.) All systems consisting of the two hylotropic [1] isomeric susbtances α and β will, therefore, ultimately frecze at the point D, which is called the " natural " freezing-point [2] of the system ; provided, of course, that sufficient time is allowed for equilibrium to be established. From this it is apparent that *the stable modification at temperatures in the neighbourhood of the melting-point is that which is in equilibrium with the liquid phase at the natural freezing-point.*

From what has been said, it will be easy to predict what will be the behaviour of the system under different conditions. If pure α is heated, a temperature will be reached at which it will melt, but this melting-point will be sharp only if the velocity of isomeric transformation is comparatively slow ; *i.e.* slow in comparison with the determination of the melting-point. If the substance be maintained in the fused condition for some time, a certain amount of the β-modification will be formed, and on lowering the temperature the pure α-form will be deposited, not at the temperature of the melting-point, but at some lower temperature depending on the concentration of the β-modification in the liquid phase. If isomeric transformation takes place slowly in comparison with the rate at which deposition of the solid occurs, the liquid will become increasingly rich in the β-modification, and the freezing-point will, therefore, sink continuously. At the eutectic point, however, the β-modification will also be deposited, and the temperature will remain constant until all has become solid. If, on the other hand, the velocity of transformation is sufficiently rapid, then as quickly as the α-modification is deposited, the equilibrium between the two isomeric forms in the liquid phase will continuously readjust itself, and the endpoint of solidification will be the natural freezing-point.

Similarly, starting with the pure β-modification, the freezing-point after fusion will gradually fall owing to the formation of the α-modification ; and the composition of the liquid phase will pass along the curve BC. If, now, the rate of cooling is not too great, or if the velocity of isomeric transformation is sufficiently rapid, complete solidification will not occur at the eutectic point ; for at this temperature solid and liquid are not in stable equilibrium with one another. On the contrary, a further quantity of the β-modification will undergo isomeric change, the liquid phase will become richer in the α-form, and the freezing-point will *rise ;* the solid phase in contact with the liquid being now the α-modification. The freezing-point will continue to rise until the point D is reached, at which complete solidification will take place without further change of temperature.

The diagram also allows us to predict what will be the result of rapidly cooling a fused mixture of the two isomerides. Suppose that either the α- or the β-modification has been maintained in the fused

[1] Hylotropic substances are such as can undergo transformation into other substances of the same composition (Ostwald, *Lehrbuch*, II., **2**, 298).

[2] Also called Equilibrium Point (Lowry).

state at the temperature t' sufficiently long for equilibrium to be established. The composition of the liquid phase will be represented by x'. If the liquid is now *rapidly* cooled, the composition will remain unchanged as represented by the dotted line x'G. At the temperature of the point G solid α-modification will be deposited. If the cooling is not carried below the point G, so as to cause complete solidification, the freezing-point will be found to rise with time, owing to the conversion of some of the β-form into the α-form in the liquid phase; and this will continue until the composition of the liquid has reached the point D. From what has just been said, it can also be seen that if the freezing-point curves can be obtained by actual determination of the freezing-points of different synthetic mixtures of the two isomerides, it will be possible to determine the condition of equilibrium in the fused state at any given temperature without having recourse to analysis. All that is necessary is to cool rapidly the fused mass, after equilibrium has been established, and to find the freezing-point at which solid is deposited; that is, find the point at which the line of constant temperature cuts the freezing-point curve. The composition corresponding to this temperature gives the composition of the equilibrium mixture at the given temperature.

It will be evident, from what has gone before, that the degree of completeness with which the different curves can be realised will depend on the velocity with which isomeric change takes place, and on the rapidity with which the determinations of the freezing-point can be carried out. As the two extremes we have, on the one hand, practically instantaneous transformation, and on the other, practically infinite slowness of transformation. In the former case, only one melting- and one freezing-point will be found, viz. the natural freezing-point; in the latter case, the two isomerides will behave as two perfectly independent components, and the equilibrium curve DE will not be realised.

An examination of Fig. 63 will show that under favourable conditions the less stable form may separate from the equilibrium mixture. If the homogeneous equilibrium curve DE slopes as shown in the figure, and cuts the curve AC for the α-modification not very far from the eutectic point; and if, on lowering the temperature through the point D, supercooling takes place and the stable form does not separate out, it may be possible to cool the liquid down to the point D′ where the equilibrium curve cuts the metastable prolongation of the curve BC, and the less stable, or β-modification, may then crystallise out.

The diagram which is obtained when isomeric transformation does not occur within measurable time at the temperature of the melting-point is somewhat different from that already given in Fig. 62. In this case, the two freezing-point curves AC and BC (Fig. 64) can be readily realised, as no isomeric change occurs in the liquid phase. Suppose, however, that at a higher temperature, t', reversible isomeric transformation can take place, the composition of the liquid phase will alter until at the point x' a condition of equilibrium is reached;

and the composition of the liquid at higher temperatures will be represented by the curve x'F. Below the temperature t' the position of the equilibrium curve is hypothetical; but as the temperature falls the velocity of transformation diminishes, and at last becomes *practically* zero. The equilibrium curve can therefore be regarded as dividing into two branches, x'G and x'H. At temperatures between G and t' the α-modification can undergo isomeric change leading to a point on the curve Gx'; and the β-modification can undergo change leading to a point on the curve Hx'. The same condition of equilibrium is therefore not reached from each side, and we are therefore dealing not with true, but with false equilibrium (p. 4). Below the temperatures G and H, isomeric transformation does not occur in measurable time. We shall not, however, enter into a detailed discussion of the equilibria in such systems, more especially as they are not systems in

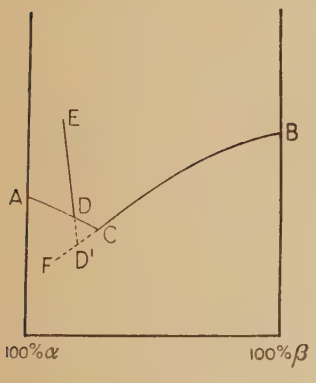


FIG. 63.

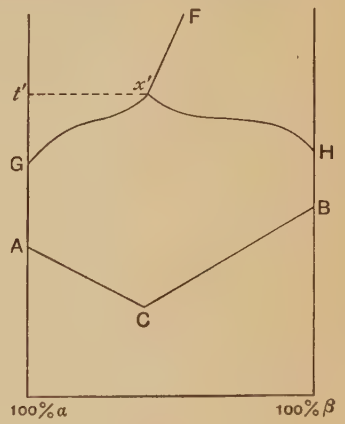


FIG. 64.

true equilibrium, and as the temperature at which true equilibrium can be established with appreciable velocity alters under the influence of catalytic agents.[1] Examples of such systems will no doubt be found in the case of optically active substances, where both isomerides are apparently quite stable at the melting-point. In the case of such substances, also, the action of catalytic agents in producing isomeric transformation (racemisation) is well known.

Transformation of the Unstable into the Stable Form.—As has already been stated, the stable modification in the neighbourhood of the melting-point is that one which is in equilibrium with the liquid phase at the natural freezing-point. In the case of polymorphic substances, we have seen (p. 56) that that form which is stable in the neighbourhood of the melting-point melts at the higher temperature. That was a consequence of the fact that the two polymorphic forms

[1] For a discussion of these systems, see Roozeboom, *Z. physikal. Chem.*, 1899, **28**, 288.

on melting give identical liquid phases. In the present case, however, the above rule does not apply, for the simple reason that the liquid phase obtained by the fusion of the one modification is not identical with that obtained by the fusion of the other. In the case of isomeric substances, therefore, the form of lower melting-point *may* be the more stable; and where this behaviour is found it is a sign that the two forms are isomeric (or polymeric) and not polymorphic.[1] An example of this is found in the case of the isomeric benzaldoximes.

Since in Fig. 62 the α-modification has been represented as the stable form, the transformation of the β into the α form will be possible at all temperatures down to the transition point. At temperatures below the eutectic point, transformation will occur without formation of a liquid phase; but at temperatures above the eutectic point liquefaction can take place. This will be more readily understood by drawing a line of constant temperature, HK, at some point between C and B. Then, if the β-modification is maintained for a sufficiently long time at that temperature, a certain amount of the α-modification will be formed; and when the composition of the mixture has reached the point H, fusion will occur. If the temperature is maintained constant, isomeric transformation will continue to take place in the liquid phase until the equilibrium point for that temperature is reached. If this temperature is higher than the natural melting-point, the mixture will remain liquid all the time; but if it is below the natural melting-point, then the α-modification will be deposited when the system reaches the condition represented by the point on the curve AC corresponding to the particular temperature. As isomeric transformation continues, the freezing-point of the system will rise until it reaches the natural freezing-point, or unary freezing-point, as it is also called, D. Similarly, if the α-modification is maintained at a temperature above that of the point D, liquefaction will ultimately occur, and the system will again reach the final state represented by D.[2]

[1] See Bancrott, *J. Physical Chem.*, 1898, **2**, 143; Wegscheider, *Sitzungsber. Wiener Akad.*, 1902, **110**, 908.

[2] Reference may be made here to the term "stability limit," introduced by Knorr (*Annalen*, 1896, **293**, 88) to indicate that temperature above which liquefaction and isomeric change takes place. As employed by Knorr and others, the term does not appear to have a very precise meaning, since it is used to denote, not the temperature at which these changes *can* occur, but the temperature at which the change is rapid (vide *Annalen*, 1896, **293**, 91; 1899, **306**, 334); and the introduction of an indefinite velocity of change renders the temperature of the stability limit also somewhat indefinite. The definiteness of the term is also not a little diminished by the fact that the "limit" can be altered by means of catalytic agents. Since, as we have seen, the stable modification *can* always undergo isomeric change and liquefy at temperatures above the natural freezing-point, but *not* below that point; and, further, since the less stable modification can undergo isomeric transformation and liquefy at temperatures above the eutectic point, but will not liquefy at temperatures below that, it seems to the author that it would be more precise to identify these two points—the natural freezing-point and the eutectic point—which are not altered by catalytic agents, with the "stability limits" of the stable and unstable modification respectively. A perfectly definite meaning would thereby be given to the term. In the case of those substances which do not undergo appreciable isomeric change at the temperature of the melting-point, the stability limits would be the points G and H (Fig. 64).

Examples.—*Benzaldoximes.* The relationships which have just been discussed from the theoretical point of view will be rendered clearer by a brief description of cases which have been experimentally investigated. The first we shall consider is that of the two isomeric benzaldoximes :—[1]

$$\begin{matrix} C_6H_5 . C . H \\ \| \\ HO . N \end{matrix}$$

Benzantialdoxime (α-modification).

$$\begin{matrix} C_6G_5 . C . H \\ \| \\ N . OH \end{matrix}$$

Benzsynaldoxime (β-modification).

Fig. 65 gives a graphic representation of the results obtained.

The melting-point of the α-modification is 34°—35° ; the melting-point of the unstable β-modification being 130°. The freezing curves AC and BC were obtained by determining the freezing-points of different mixtures of known composition, and the numbers so obtained are given in the following table :—

Grams of the α-modification in 100 gm. of mixture.	Freezing-point.
26·2	101°
49·2	79°
73·7	46°
91·7	26·2°
95·0	28·6°
96·0	30·0°

The eutectic point C was found to lie at 25°—26°, and the natural freezing-point D was found to be 27·7°. The equilibrium curve DE was determined by heating the liquid mixtures at different temperatures until equilibrium was attained, and then rapidly cooling the liquid. In all cases the freezing-point was practically that of the point D. From this it is seen that the equilibrium curve must be a straight line parallel to the temperature axis; and, therefore, isomeric transformation in the case of the two benzaldoximes is not accompanied by any heat effect (p. 146). This behaviour has also been found in the case of acetaldoxime.[2]

The isomeric benzaldoximes are also of interest from the fact that the stable modification has the *lower* melting-point (*v.* p. 150).

Acetaldehyde and Paraldehyde.—As a second example of the equilibria between two isomerides, we shall take the two isomeric (polymeric) forms of acetaldehyde, which have been exhaustively studied.[3]

[1] Cameron, *J. Physical Chem.*, 1898, **2**, 409; Schoevers, *Dissertation*, Amsterdam, 1907.

[2] Carveth, *J. Physical Chem.*, 1898, **2**, 159. See also Dutoit and Fath, *J. Chim. phys.*, 1903, **1**, 358; Findlay, *J. Chem. Soc.*, 1904, **85**, 403.

[3] Hollmann, *Z. physikal. Chem.*, 1903, **43**, 129.

In the case of these two substances the reaction

$$3CH_3 . CHO \leftrightarrows (CH_3 . CHO)_3$$

takes place at the ordinary temperature with very great slowness. For this reason it is possible to determine the freezing-point curves of acetaldehyde and paraldehyde. The three chief points on these curves, represented graphically in Fig. 66, are :—

m.p. of acetaldehyde	− 118·45°
m.p. of paraldehyde	+ 12·55°
eutectic point	− 119·9°

In order to determine the position of the natural melting-point, it was necessary, on account of the slowness of transformation, to employ a

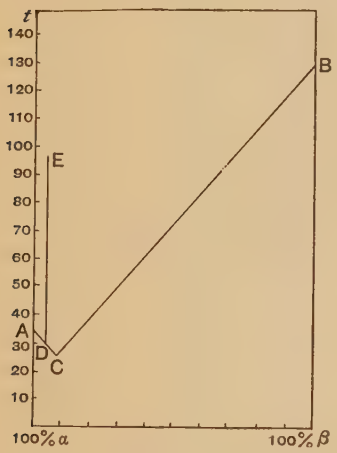


Fig. 65.

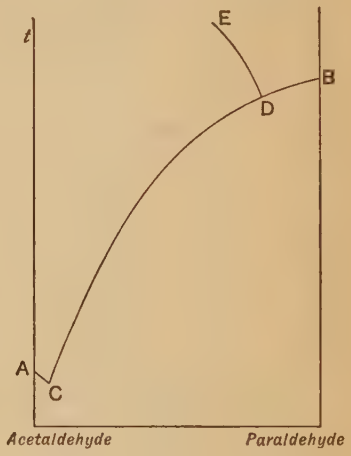


Fig. 66.

catalytic agent in order to increase the velocity with which the equilibrium was established. A drop of concentrated sulphuric acid served the purpose. In presence of a trace of this substance, isomeric transformation very speedily occurs, and leads to the condition of equilibrium. Starting in the one case with fused paraldehyde, and in the other case with acetaldehyde, the same freezing-point, viz. 6·75°, was obtained, the solid phase being paraldehyde. This temperature, 6·75°, is therefore the natural freezing-point, and paraldehyde, the solid in equilibrium with the liquid phase at this point, is the stable form.

With regard to the change of equilibrium with the temperature, it was found that whereas the liquid phase contains 11·7 molecules per cent. of acetaldehyde at the natural freezing-point, the liquid at the temperature of 41·6° contains 46·6 molecules per cent. of acetaldehyde. As the temperature rises, therefore, there is increased formation of acetaldehyde, or a decreasing amount of polymerisation. This is in

harmony with the fact that the polymerisation of acetaldehyde is accompanied by evolution of heat.

While speaking of these isomerides, it may be mentioned that at the temperature 41·6° the equilibrium mixture has a vapour pressure equal to the atmospheric pressure. At this temperature, therefore, the equilibrium mixture (obtained quickly with the help of a trace of sulphuric acid) boils.[1]

From a more recent investigation by Smits and de Leeuw,[2] it would, however, appear probable that the acetaldehyde-paraldehyde system is not so simple as was found by Hollmann, but that we have here a case of a pseudo-ternary system in which are present not only the simple acetaldehyde molecules ($CH_3 . CHO$), but also the molecules of paraldehyde, $(CH_3 . CHO)_3$, and of metaldehyde, $(CH_3 . CHO)_4$.

Sulphur.

It has already been indicated (p. 53), that in the case of sulphur we have a substance which can give rise to different molecular species which, in the liquid state, form an equilibrium mixture. For this reason, sulphur will behave not as a purely unary system, but in a manner similar to that of dynamic isomerides discussed in this chapter. We shall therefore discuss briefly the more important equilibrium relations of sulphur from this point of view.

Melting Points of Sulphur.—When sulphur is heated to above its melting-point it fuses to an amber-coloured, mobile liquid, which passes, as the temperature is raised, into a dark brown viscous liquid. This peculiar behaviour of sulphur was attributed by A. Smith and his collaborators [3] to the existence in molten sulphur of two modifications, S_λ and S_μ, in dynamic equilibrium. Of these two modifications, S_λ is soluble in carbon disulphide, and is the normal molecular form corresponding with the crystalline rhombic or monoclinic sulphur. It is the form which is first produced when crystalline sulphur is melted. S_μ, on the other hand, is insoluble in carbon disulphide, and is formed in increasing quantity as the temperature is raised.[4] Molten sulphur, therefore, is not a pure liquid consisting of only one kind of molecules, but is a homogeneous mixture or solution of S_μ in S_λ, the composition of which varies with the temperature. The attainment of equilibrium is accelerated by the presence of traces of ammonia, and is retarded by the presence of sulphur dioxide.

The views expressed by Smith and his collaborators regarding the nature of molten sulphur have been modified and extended by A. H. W.

[1] For other examples of the application of the Phase Rule to isomeric substances, see *J. Physical Chem.*, vol. **2** *et seq.*; Findlay, *J. Chem. Soc.*, 1904, **85**, 403; Atkins and Werner, *ibid.*, 1912, **101**, 1167; Smits and Kettner, *Proc. K. Akad. Wetensch., Amsterdam*, 1912, **15**, 683; Dutoit and Fath, *J. Chim. phys.*, 1903, **1**, 358.

[2] *Z. physikal. Chem.*, 1911, **77**, 269.

[3] *J. Amer. Chem. Soc.*, 1905, **27**, 801, 983; *Z. physikal. Chem.*, 1903, **42**, 469; 1905, **52**, 602; 1906, **54**, 257; 1907, **57**, 685; 1907, **61**, 200, 209.

[4] Smith and Carson, *Z. physikal. Chem.*, 1907, **57**, 685.

Aten,[1] according to whom there exist in molten sulphur not only the S_λ and S_μ molecules, but also another molecular species, S_π,[2] which is readily soluble in carbon disulphide. At each temperature there exists, in molten sulphur, an equilibrium between these three molecular species in accordance with the numbers shown in the following table :—

EQUILIBRIUM BETWEEN S_λ, S_μ, AND S_π IN MOLTEN SULPHUR.

Temperature.	Per cent. S_μ.	Per cent. S_π.	Per cent. S_λ.
120°	0·1	3·5	96·4
125°	0·2	4·1	95·7
130°	0·3	4·3	95·4
140°	1·3	5·0	93·7
145°	1·6	5·3	93·1
160°	4·1	6·7	89·2
170°	13·3	5·8	80·9
180°	20·4	6·5	73·1
184°	23·6	6·3	70·1
196°	28·6	6·3	65·1
220°	32·2	5·3	62·7
445°	36·9	4·0	59·1

In the solidified melt, S_π changes very rapidly into S_μ, which, in turn, is transformed slowly into the normal S_λ.

The occurrence of " dynamic allotropy " in the case of liquid sulphur is of great importance for the quantitative study of the equilibrium between solid and liquid sulphur. Since, in the case of molten sulphur, we are dealing with a homogeneous mixture of three molecular species, S_λ, S_μ, and S_π, from which solid, soluble sulphur, corresponding with S_λ, crystallises out, it follows that the system will no longer behave like a one-component or unary system, but rather will simulate the behaviour of a three-component or ternary system. The system may therefore be said to be a pseudo-ternary system. If, however, for the sake of simplicity we group the two molecular species S_μ and S_π as one, we can treat the system as a pseudo-binary one ; and this method of treatment is justified by the fact that in the neighbourhood of the freezing-point of molten sulphur, S_μ is present in very small amount and may be neglected.

From what has just been said, therefore, we see that the equilibrium relations between crystalline sulphur and liquid sulphur will be similar to those found in the case of dynamic isomerides. As in the case of such substances, the crystalline forms of sulphur may exhibit various melting- or freezing-points, and only when there is complete absence of the molecular species S_π or S_μ do we obtain the ideal or true freezing-point ; that is, the equilibrium temperature between crystalline sulphur

[1] *Z. physikal. Chem.*, 1912, **81**, 257 ; 1913, **83**, 442 ; 1913, **86**, 1 ; 1914, **88**, 321.

[2] S_λ is regarded as having a molecular weight represented by S_8 ; S_π a molecular weight represented by S_4.

and molten S_λ. Under ordinary conditions, the melting-point is found lower than the ideal melting-point, owing to the formation of and presence in the molten sulphur of S_π.[1] The natural freezing-point is therefore the temperature at which crystalline sulphur coexists with the equilibrium mixture of S_λ and S_π.

The following values for the ideal and natural freezing-point of rhombic (S_I), monoclinic (S_{II}), and mother of pearl sulphur (S_{III}) are given in the following table :—[2]

Solid phase.	Ideal freezing-point.	Natural freezing-point.
Rhombic sulphur (S_I) . .	112·8°	110·2°
Monoclinic sulphur (S_{II}) . .	119·25° (118·95°)	114·5°
Mother of pearl sulphur (S_{III}) .	106·8°	103·4°

As a result of the recent investigations of the pseudo-binary systems of the substance sulphur we obtain the diagram shown in Fig. 67. Here, the points A, D, and G represent the ideal freezing-points of monoclinic, rhombic, and nacreous sulphur respectively, or the temperatures at which these three crystalline forms are in equilibrium with pure molten S_λ. The curve HEB represents the dynamic equilibrium curve for S_λ, S_μ, and S_π in molten sulphur ; and the points B, E, and H, where this equilibrium curve cuts the freezing-point curves, represent the natural freezing-points of the three modifications of sulphur.

The above facts are of essential importance in connection with the equilibrium diagrams of sulphur, Fig. 13 (p. 54) and Fig. 14 (p. 56). In these figures, the data represented in the diagram relate neither to the "ideal" equilibrium conditions in which the solid phase is in equilibrium with S_λ, nor to the "natural" equilibrium conditions in which the solid phase is in equilibrium with the equilibrium mixture of S_λ, S_μ, and S_π; they refer, rather, to conditions in which unknown

[1] The view put forward by Aten (*loc. cit.*) that in the neighbourhood of the freezing-point molten sulphur consists essentially of the molecular species S_λ and S_π (see Table on p. 154), and that the lowering of the melting-point of sulphur is due to the presence of S_π, and not of S_μ as was thought by Smith and Carson, has been confirmed, cryoscopically, by Beckmann, Paul, and Liesche (*Z. anorgan. Chem.*, 1918, **103**, 189). According to these investigators, the composition of the melt at the natural freezing-point is $S_\pi = 2{\cdot}78$ per cent., $S_\lambda = 97{\cdot}22$ per cent. So-called amorphous sulphur, S_μ, when added to molten sulphur at the natural freezing-point does not alter the freezing-point of the melt, owing to the fact that it undergoes a rapid transformation into the equilibrium mixture of S_λ and S_π. Another molecular form of sulphur, Engel's sulphur or S_ρ, obtained by the action of hydrochloric acid on sodium thiosulphate (Engel, *Compt. rend.*, 1891, **112**, 866), and having the molecular weight of 192 (S_6), when added to the equilibrium mixture, lowers the freezing-point ; but S_ρ also undergoes transformation into S_λ and S_π by way of S_μ.

[2] Smith and Carson, *Z. physikal. Chem.*, 1911, **77**, 670. See also Kruyt, *ibid.*, 1909, **67**, 338 ; 1912, **81**, 726 ; Wigand, *ibid.*, 1910, **75**, 242 ; Aten, *ibid.*, 1912, **81**, 257 ; Smits, *ibid.*, 1913, **83**, 221 ; Nernst, *ibid.*, 1913, **83**, 546 ; de Leeuw, *ibid.*, 1913, **83**, 245.

and variable amounts of S_μ and S_π are present in the liquid phase. The actual values found by Tammann, therefore, for the curves *b*C, CD, BC, which are represented in Figs. 13 and 14, are not quite correct, although they may be taken as representing qualitatively the relationships involved.

On the basis of his theory of allotropy, according to which there separates from a liquid mixture in dynamic equilibrium, not a pure solid substance but a solid phase consisting also of an equilibrium mixture (a solid solution), Smits [1] has suggested a diagram for the equilibrium relations of sulphur. This diagram, however, has not yet

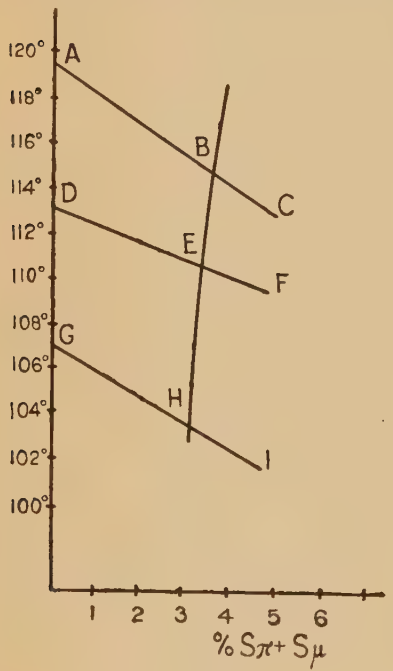


FIG. 67.

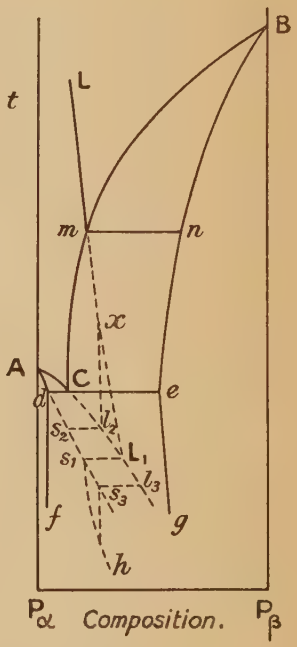


FIG. 68.

been fully tested experimentally, and the theoretical basis on which it has been constructed is not free from criticism.[2]

Phosphorus as Pseudo-binary System.—For the purpose of illustrating the behaviour of a one-component system as interpreted by means of the theory of allotropy put forward by Smits, a brief discussion of the behaviour of phosphorus may be given.[3]

[1] *Z. physikal. Chem.*, 1913, **83**, 221; *Die Theorie der Allotropie* (Barth, 1921). See also de Leeuw, *Z. physikal. Chem.*, 1913, **83**, 245.

[2] Tammann, *Z. physikal. Chem.*, 1913, **83**, 728; **84**, 753. See also Smith and Carson, *ibid.*, 1907, **57**, 695.

[3] Smits and Bokhorst, *Z. physikal. Chem.*, 1916, **91**, 249.

According to the theory of Smits, phosphorus exists in two molecular species between which, under normal conditions, an inner equilibrium obtains, not only in the liquid but also in the solid state. These molecular species or pseudo-components may be called the α and β forms of phosphorus (P_α and P_β). The various "allotropic modifications," such as white phosphorus and violet phosphorus, are to be regarded as solid solutions of P_α and P_β in different percentage amounts.

Evidence for the complexity of phosphorus is found in the fact that although it behaves as a unary substance when temperature changes are carried out slowly (so as to allow of inner equilibrium being established), it no longer does so when the temperature changes are rapid. Thus, when white phosphorus is heated slowly, the melting-point 44° is found, but if heated rapidly the melting-point is below 44°. Again, if molten phosphorus is rapidly cooled, the freezing-point varies with the temperature from which the liquid is cooled and the rapidity of cooling.

On the basis of Smits' theory, the behaviour of phosphorus can be interpreted by means of the diagram shown in Fig. 68.[1]

A and B are the imaginary melting-points of pure P_α and P_β. In equilibrium with the liquid solutions AC there exist the solid solutions *Ad*; and in equilibrium with the liquid solutions BC, there exist the solid solutions *Be*. Below the eutectic horizontal *de* lies the metastable equilibrium diagram for the solid solutions ($s_2 s_1 s_3$), known as white phosphorus, in contact with liquid solutions, $l_2 L_1 l_3$. $Lx L_1$ is the curve of internal equilibrium in molten phosphorus. At *m*, molten phosphorus deposits (if supercooling is excluded) the solid solution *n* (violet phosphorus). The temperature corresponding to *m* is about 590° (p. 62).

If molten phosphorus is slowly cooled, so as to allow the internal equilibrium to be established, and if separation of violet phosphorus does not take place, the composition of the liquid will follow the line $Lx L_1$. At L_1 (44°), separation of the solid solution s_1 (white phosphorus) takes place.

If, at the temperature corresponding with *x*, the liquid be rapidly cooled, separation of solid solution, s_2, will take place at the temperature corresponding with l_2. That is, the freezing-point varies with the rapidity of cooling. Further, the solid solution s_1 is an equilibrium mixture of P_α and P_β, and this equilibrium may alter with the temperature, as shown by the line $s_1 h$. Consequently, if white phosphorus is heated rapidly from a low temperature after the internal equilibrium has been established, the melting-point will not be s_1, but, say, s_3. The diagram enables one, therefore, on the basis of the theory put forward by Smits, to account for the variation of physical properties, *e.g.* melting-point, with the past history and treatment of the substance.

[1] This has been somewhat simplified in order to bring out only the essential points of the theory concerning white and violet phosphorus.

CHAPTER XI.

SYSTEMS OF TWO COMPONENTS (*Continued*).

D. Coexistence of Solid, Liquid, and Gas Phases.

I. Only one of the Components is Volatile.

In the present chapter it is proposed to discuss the application of the Phase Rule to the study of two-component systems in which one of the components is volatile. Attention will be confined mainly to those systems in which the volatile component is water. It must not, however, be thought that these systems differ essentially from the systems already discussed—although differences in detail are no doubt present—but they are given a separate treatment here not only by reason of their great importance, but also because, in the case of these systems, the attention is directed very largely to only a portion of the equilibrium diagram; to that portion, namely, which relates to systems in which water, or other volatile component, is present in relatively large amount. In other words, interest centres largely, although not exclusively, on that part of the equilibrium diagram which is spoken of ordinarily as the solubility curve.

When one determines the equilibria in the system water—silver nitrate under atmospheric pressure, the following numbers are obtained :—[1]

Water and Silver Nitrate.

Temperature.	Solid phase.	Composition of solution (grams of $AgNO_3$ in 100 grams of solution).
— 5·6°	Ice.	34·2
— 7·3°	Ice + $AgNO_3$ (rhombic).	47·1
0°	$AgNO_3$ (rhombic).	53·5
+ 10°	,,	61·5
20°	,,	68·3
40°	,,	77·0
80°	,,	86·7
110°	,,	91·7
133°	,,	95·1
208·6°	$AgNO_3$ (rhombohed.) — m.p.	100·0

[1] Middelberg, *Z. physikal. Chem.*, 1893, **43**, 313; Etard, *Annales chim. phys.*, 1894 [7], **2**, 524; Tilden and Shenstone, *Phil. Trans.*, 1884, **175**, 23; Hissink, *Z. physikal. Chem.*, 1900, **32**, 543. (See Landolt-Börnstein, *Tabellen*.)

On plotting these values in a temperature-composition diagram, the equilibrium curve shown diagrammatically in Fig. 69 is obtained. This diagram, it will be seen, is similar to that shown in Fig. 33 (p. 103), and consists of two branches intersecting at a eutectic point, at which the two solid components are in equilibrium with solution.[1] Along the one branch of the curve, from 0° to — 7·3°, ice exists in equilibrium with solution, the freezing-point of water being lowered by the presence of the silver nitrate. The other branch of the curve represents the composition of solutions in equilibrium with silver nitrate as solid phase, the freezing-point of fused silver nitrate being lowered by the presence of water. At the point of intersection of these two curves, at a temperature of — 7·3°, both solid components, ice and silver nitrate, coexist in equilibrium with a solution of definite composition. This is the eutectic point.

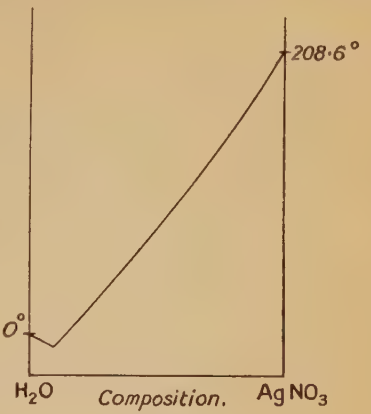


FIG. 69.

Cryohydric Point and Cryohydrates.—In the case of systems in which water is one of the components, the eutectic point long ago received the name *cryohydric point*,[2] a term which arose from a study of the freezing of salt solutions. On cooling a solution of common salt in water to a temperature of — 3°, Guthrie observed that the hydrate NaCl, $2H_2O$ separated out. This salt continued to be deposited until at a temperature of — 22° opaque crystals made their appearance, and the liquid passed into the solid state without change of temperature. A similar behaviour was found by Guthrie in the case of a large number of other salts, a temperature below that of the melting-point of ice being reached at which, on continued withdrawal of heat, the solution solidified at a constant temperature. When the system had attained this minimum temperature, it was found that the composition of the solid and the liquid phases was the same, and remained unchanged throughout the period of solidification. This is shown by the figures on the following page, which give the composition of different samples of the solid phase deposited from the solution at constant temperature.

Conversely, an intimate mixture of ice and salt containing 23·6 per cent. of sodium chloride melts at a definite and constant temperature, and exhibits, therefore, a behaviour supposed to be characteristic

[1] Attention should be drawn to the fact that silver nitrate exists in two crystalline forms, rhombic and rhombohedral, with a transition point at 159°-160°. The one branch of the curve, therefore, should exhibit a break at this temperature (p. 105).

[2] Guthrie, *Phil. Mag.*, 1875 [4], **49**, 1; 1884 [5], **17**, 462.

No.	Temperature of solidification.	NaCl per cent.
1	— 21° to — 22°	23·72
2	— 22°	23·66
3	— 22°	23·73
4	— 23°	23·82
5	— 23°	23·34
6	— 23°	23·35
	Mean . . .	23·6

of a pure chemical compound. This, then, combined with the fact that the solid which was deposited was crystalline, and that the same constant temperature was attained, no matter with what proportions of water and salt one started, led Guthrie to the belief that the solids which thus separated at constant temperature were definite chemical compounds, to which he gave the general name *cryohydrate*. A large number of such cryohydrates were prepared and analysed by Guthrie, and a few of these are given in the following table, together with the temperature of the cryohydric point:—[1]

CRYOHYDRATES.

Salt.	Cryohydric point.	Percentage of anhydrous salt in the cryohydrate.
Sodium bromide . . .	— 24°	41·33
Sodium chloride . . .	— 22°	23·60
Potassium iodide . . .	— 22°	52·07
Sodium nitrate . . .	— 17·5°	40·80
Ammonium sulphate . .	— 17°	41·70
Ammonium chloride . .	— 15°	19·27
Sodium iodide . . .	— 15°	59·45
Potassium bromide . . .	— 13°	32·15
Potassium chloride . .	— 11·4°	20·03
Magnesium sulphate . .	— 5°	21·86
Potassium nitrate . . .	— 2·6°	11·20
Sodium sulphate . . .	— 0·7°	4·55

The chemical individuality of these cryohydrates was, however, called in question by Pfaundler,[2] and disproved by Offer,[3] who showed that in spite of the constancy of the melting-point, the cryohydrates had the properties, not of definite chemical compounds, but of mix-

[1] Guthrie, *Phil. Mag.*, 1875 [4], **49**, 1, 206, 266; 1876 [5], **1**, 49, 351, 446; 1876, [5], **2**, 211.
[2] *Ber.*, 1877, **20**, 2223.
[3] *Sitz.-Ber. Wien. Akad.*, 1880, **81**, II., 1058.

tures; the arguments given being that the heat of solution and the specific volume are the same for the cryohydrate as for a mixture of ice and salt of the same composition; and it was further shown that the cryohydrate had not a definite crystalline form, but separated out as an opaque mass containing the two components in close juxtaposition. The heterogeneous nature of cryohydrates can also be shown by a microscopical examination.

At the cryohydric point, therefore, we are not dealing with a single solid phase, but with two solid phases, ice and salt; and, as we have already learned, the constancy of temperature and composition at the cryohydric or eutectic point is due to the fact that we are dealing with an invariant system.

The cryohydric or eutectic point is thus clearly seen to be the point of intersection of the solubility curve of the salt and the freezing-point curve of water. At this point, also, the curves of the univariant systems ice—salt—vapour and ice—salt—solution intersect. The cryohydric point is therefore a quadruple point, and represents an invariant system.

Changes at the Quadruple Point.—Since the invariant system ice—salt—solution—vapour can exist only at a definite temperature, addition or withdrawal of heat must cause the disappearance of one of the phases, whereby the system will become univariant. So long as all four phases are present the temperature, pressure, and concentration of the components in the solution must remain constant. When, therefore, heat is added to or withdrawn from the system, mutually compensatory changes will take place within the system whereby the condition of the latter is preserved. These changes can in all cases be foreseen with the help of the theorem of van't Hoff and Le Chatelier; and, after what was said on pages 18 and 19, need only be briefly referred to here. In the first place, addition of heat will cause ice to melt, and the concentration of the solution will be thereby altered; salt must therefore dissolve until the original concentration is reached, and the heat of fusion of ice will be counteracted by the heat of solution of the salt. Changes of volune of the solid and liquid phases must also be taken into account; an alteration in the volume of these phases being compensated by condensation or evaporation. All four phases will therefore be involved in the change, and the final state of the system will be dependent on the amounts of the different phases present; the ultimate result of addition or withdrawal of heat or of change of pressure at the quadruple point will be one of the four univariant systems: ice—solution—vapour; salt—solution—vapour; ice—salt—vapour; ice—salt—solution. If the vapour phase disappear, there will be left the univariant system ice—salt—solution, and the temperature at which this system can exist will alter with the pressure.[1] Since in this case the influence of pressure is comparatively slight, the temperature of the quadruple point will differ only slightly

[1] See footnote, p. 103.

from that of the cryohydric point as determined under atmospheric pressure.

Freezing Mixtures.—Not only will the composition of a univariant system undergo change when the temperature is varied, but, conversely, if the *composition* of the system is caused to change, corresponding changes of temperature must ensue. Thus, if ice is added to the univariant system salt—solution—vapour, the ice must melt and the temperature fall; and if sufficient ice is added, the temperature of the cryohydric point must be at length reached, for it is only at this temperature that the four phases ice—salt—solution—vapour can coexist. On the other hand, if salt is added to the system ice —solution—vapour, the concentration of the solution will increase, ice must melt, and the temperature must thereby fall; and this process also will go on until the cryohydric point is reached. In both cases ice melts and there is a change in the composition of the solution; in the former case, salt will be deposited [1] because the solubility diminishes as the temperature falls; in the latter, salt will pass into solution. This process may be accompanied either by evolution or, more generally, by absorption of heat; in the former case the effect of the addition of ice will be partially counteracted; in the latter case it will be augmented.

These principles are made use of in the preparation of *freezing mixtures*. The lowest temperature which can be reached (under atmospheric pressure) by means of these, is the cryohydric point. This temperature-minimum is, however, not always attained in the preparation of a freezing mixture, and that for various reasons. The chief of these are radiation and the heat absorbed in cooling the solution produced. The lower the temperature falls, the more rapid does the radiation become; and the rate at which the temperature sinks decreases as the amount of solution increases. Both these factors counteract the effect of the latent heat of fusion and the heat of solution, so that a point is reached (which may lie considerably above the cryohydric point) at which the two opposing influences balance. The absorption of heat by the solution can be diminished by allowing the solution to drain off as fast as it is produced; and the effect of radiation can be partially annulled by increasing the rate of cooling. This can be done by the more intimate mixing of the components. Since, under atmospheric pressure, the temperature of the cryohydric point is constant, the cryohydrates are very valuable for the production of baths of constant low temperature.

From what has been said in the preceding paragraphs, it will be clear that in the case of the system water—silver nitrate, in which no compound is formed between the components, we are dealing with a system which is in all respects analogous to the system *o*-nitrophenol—

[1] If in the neighbourhood of the cryohydric point solution should be accompanied by an evolution of heat, then as the solubility would in that case increase with fall of temperature, salt would pass into solution.

p-toluidine (p. 107), or to the system zinc—aluminium (p. 136). It is, moreover, evident that *the so-called solubility curve, or the curve which represents the composition of solutions in equilibrium with the solid solute at different temperatures, is identical with the equilibrium curve or freezing-point curve of the fused solute in presence of water.* While it is of importance always to bear this fact in mind, it is nevertheless advantageous to give separate and special consideration to the question of solubility and solubility curves, owing both to differences in experimental method and to the special interests involved in their study.

When a solid is brought into contact with a liquid in which it can dissolve, a certain amount of it passes into solution; and the process continues until the concentration reaches a definite value independent of the amount of solid present. A condition of equilibrium is established between the solid and the solution; the solution becomes *saturated*. Since the number of components is two, and the number of phases three, viz. solid, liquid solution, vapour, the system is univariant. If, therefore, one of the factors, pressure, temperature, or concentration of the components (in the solution [1]), is arbitrarily fixed, the state of the system becomes perfectly defined. Thus, at any given temperature, the vapour pressure of the system and the concentration of the components have a definite value. If the temperature is altered, the vapour pressure and also, in general, the concentration, will undergo change. Likewise, if the pressure varies, while the system is isolated so that no heat can pass between it and its surroundings, the concentration and the temperature must also undergo variation until they attain values corresponding to the particular pressure.

Considering, for the present, those systems in which only solid and liquid phases are present, it is clear that the system solid—liquid (solution) will be bivariant. If the pressure is maintained constant, the composition of the solution will vary with the temperature; or, on the other hand, if the temperature is maintained constant, the composition of the solution will vary with the pressure. The influence of temperature on the solubility of a solid in water is sufficiently appreciated; the effect of pressure, although not so well known, is no less certain.

The direction in which change of concentration will occur with change of pressure can be predicted by means of the theorem of Le Chatelier, if it is known whether increase or diminution of volume takes place when the substance dissolves in an almost saturated solution. If diminution of the total volume of the system occurs on solution, increase of pressure will increase the solubility; in the reverse case, increase of pressure will diminish the solubility.

The effect of pressure on the solubility, to which attention was long ago directed by Sorby,[2] has been made the subject of both

[1] Since this is the only phase of variable composition present.
[2] *Proc. Roy. Soc.*, 1863, **12**, 538; *Phil. Mag.*, 1864, **27**, 145.

mathematical and experimental investigation. On the basis of thermodynamics, Braun [1] derived the expression

$$\left(\frac{\partial x}{\partial \pi}\right)_T \Big/ \left(\frac{\partial x}{\partial T}\right)_\pi = -\frac{T \cdot \Delta v}{Q}.$$

In this expression, generally known as Braun's law, $\left(\frac{\partial x}{\partial \pi}\right)_T$ is the change of solubility with the pressure when the temperature is constant; $\left(\frac{\partial x}{\partial T}\right)_\pi$ is the change of solubility with the temperature when the pressure is constant; T is the absolute temperature at which the solubility is determined; Δv is the (fictitious) volume change which accompanies the solution of 1 gram-molecule of the solute in an infinitely large quantity of the saturated solution at T°; and Q is the amount of heat developed in the process. Q is equal to the so-called fictitious or ideal or last heat of solution, with sign reversed.[2]

The first experimental determinations of the effect of pressure on solubility were made by E. von Stackelberg,[3] who obtained values which are in qualitative agreement with Braun's law and the theorem of Le Chatelier, as the following table shows :—

Salt.	Change of volume by dissolving 1 gm. of salt in the saturated solution.	Solubility at 18° (grams salt in 1 gram of solution).	
		Pressure = 1 atm.	Pressure = 500 atm.
Sodium chloride . . .	− 0·07	0·264	0·270
Ammonium chloride . .	+ 0·10	0·272	0·258
Alum	− 0·067	0·115	0·142 (p = 400 atm.)

More accurate determinations of the influence of pressure on solubility, extending over a greater range of pressure, have been carried out by Cohen and his collaborators,[4] who have also tested quantitatively and have confirmed Braun's law. Some of their results are given in the following tables :—

[1] *Z. physikal. Chem.*, 1887, **1**, 258; *Annalen d. Physik*, 1887, **30**, 250. See also Cohen and Moesveld, *Z. physikal. Chem.*, 1919, **93**, 385; Sill, *J. Amer. Chem. Soc.*, 1916, **38**, 2632; Cohen, *Physico-chemical Metamorphosis and Problems in Piezochemistry*.

[2] See also footnote, p. 167.

[3] *Z. physikal. Chem.*, 1896, **20**, 337.

[4] Cohen and Sinnige, *Z. physikal. Chem.*, 1909, **67**, 432; Cohen, Inouye and Euwen, *ibid.*, 1910, **75**, 257; Cohen and Moesveld, *ibid.*, 1919, **93**, 385; Cohen, Voller, and Moesveld, *ibid.*, 1923, **104**, 323; Cohen, Ishikawa, and Moesveld, *ibid.*, 1923, **105**, 155; Cohen, Hetterschij, and Moesveld, *ibid.*, 1920, **94**, 210; Cohen, de Meester, and Moesveld, *ibid.*, 1924, **114**, 321; Cohen and van den Bosch, *ibid.*, 1925, **114**, 453. See also Cohen, *Physico-chemical Metamorphosis and Problems in Piezochemistry*.

Pressure in atm.	Solubility of mannitol at 24·05° (grams of solute in 100 grams of water).	Solubility of thallous sulphate at 30·00° (grams of solute in 100 grams of saturated solution).	Solubility of naphthalene in tetrachlorethane at 30·00° (grams of solute in 100 grams of solution).
1	20·66	5·83	35·07
250	20·92	—	30·26
500	21·14	7·48	26·40
1000	21·40	9·03	20·89
1500	21·64	10·50	—

Pressure.	Solubility of *m*-dinitrobenzene in ethyl acetate at 30·00° (grams of solute in 100 grams of solvent).
0	52·54
100	49·97
220	47·06
300	45·39
480	42·02

The values of Δv for thallous sulphate—water, naphthalene—tetrachlorethane, and *m*-dinitrobenzene—ethylacetate are $-0{\cdot}0491$, $+0{\cdot}1313$, and $+0{\cdot}0442$ c.c. per gram respectively.

From the values of the solubility, more especially of *m*-dinitrobenzene in ethylacetate and of naphthalene in tetrachlorethane, it will be clear that the pressure may, in some cases, bring about a very considerable change in the solubility. For all practical purposes, however, the solubility determined under atmospheric pressure may be taken as equal to the solubility when the system is under the pressure of its own vapour.

The Saturated Solution.—From what has been said above, it will be seen that the condition of saturation of a solution can be defined only with respect to a certain solid phase; if no solid is present, the system is undefined, for it then consists of only two phases, and is therefore bivariant. Under such circumstances not only can there be at one given temperature solutions of different concentration, all containing less of one of the components than when that component is present in the solid form, but there can also exist solutions containing more of that component than corresponds to the equilibrium when the solid is present. In the former case the solutions are *unsaturated*, in the latter case they are *supersaturated with respect to a certain solid phase;* in themselves, the solutions are stable, and are neither unsaturated nor supersaturated. Further, if the solid substance can exist in different allotropic modifications, the particular form of the substance which is in equilibrium with the solution must be known, in order that the statement of the solubility may be definite; for each

form has its own solubility, and, as we shall see presently, the less stable form has the greater solubility (*cf.* p. 60). In all determinations of the solubility, therefore, not only must the concentration of the components in the solution be determined, but equal importance should be attached to the characterisation of the solid phase present.

In this connection, also, one other point may be emphasised. For the production of the equilibrium between a solid and a liquid, time is necessary, and this time not only varies with the state of division of the solid and the efficiency of the stirring, but is also dependent on the nature of the substance.[1] Considerable care must therefore be taken that sufficient time is allowed for equilibrium to be established. Such care is more especially needful when changes may occur in the solid phase, and neglect of it has greatly diminished the value of many of the older determinations of solubility.

Form of the Solubility Curve.—The solubility curve—that is, the curve representing the change of concentration of the components in the solution with the temperature—differs markedly from the curve of vapour pressure (p. 15), in that it possesses no general form, but may vary in the most diverse manner. Not only may the curve have an almost straight and horizontal course, or slope or curve upwards at varying angles; but it may even slope downwards, corresponding to a decrease in the solubility with rise of temperature; may exhibit maxima or minima of solubility, or may, as in the case of some hydrated salts, pass through a point of maximum temperature. In the latter case the salt may possess two values of solubility at the same temperature. We shall consider these cases later.

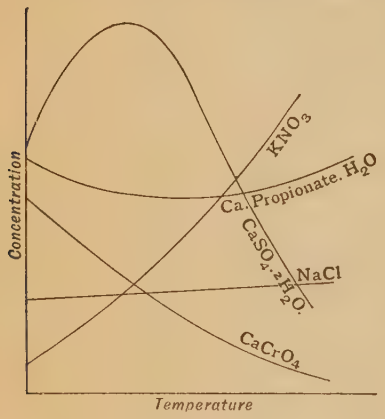


FIG. 70.

The great variety of form shown by solubility curves is at once apparent from Fig. 70, in which the solubility curves of various substances (not, however, drawn to scale) are reproduced.[2]

Varied as is the form of the solubility curve, its *direction*, nevertheless, can be predicted by means of the theorem of van't Hoff and Le Chatelier; for in accordance with that theorem (p. 18) increase of solubility with the temperature must occur in those cases where the process of solution is accompanied by an *absorption* of heat; and a decrease in the solubility with rise of temperature will be found in

[1] Van't Hoff, *Arch. néerland*, 1901 [2], **6**, 471.

[2] Tilden and Shenstone, *Phil. Trans.*, 1884, **175**, 23; Hulett and Allen, *J. Amer. Chem. Soc.*, 1902, **24**, 667; Andreæ, *J. prak. Chem.*, 1884, **137**, 474; Lumsden, *J. Chem. Soc.*, 1902, **81**, 350; Mylius and v. Wrochem, *Ber.*, 1900, **333**, 689.

cases where solution occurs with *evolution* of heat. Where there is no heat effect accompanying solution, change of temperature will be without influence on the solubility; and if the sign of the heat of solution changes, the direction of the solubility curve must also change, *i.e.* must show a maximum or minimum point. This has in all cases been verified by experiment.[1]

In applying the theorem of Le Chatelier to the course of the solubility curve, it should be noted that by heat of solution there is meant not the heat effect produced by dissolving the salt in a large amount of solvent (which is the usual signification of the expression), but the heat which is absorbed or evolved when the salt is dissolved in the almost saturated solution (the so-called last or fictitious heat of solution). Not only does the heat effect in the two cases have a different value, but it may even have a different sign. A striking example of this is afforded by cupric chloride, as the following figures show:—[2]

Number of gram-molecules of $CuCl_2$, $2H_2O$ dissolved in 198 gram-molecules of water.	Heat effect.
1	+ 37 K
2·02	+ 66 ,,
4·15	+ 105 ,,
7·07	+ 117 ,,
9·95	+ 117 ,,
11	+ 91 ,,
18·8	− 10 ,,
19·6	− 31 ,,
24·75	− 198 ,,

In the above table the positive sign indicates evolution of heat, the negative sign, absorption of heat; and the values of the heat effect are expressed in centuple calories. Judging from the heat effect produced on dissolving cupric chloride in a large bulk of water, we should predict that the solubility of that salt would diminish with rise of temperature; as a matter of fact, it increases. This is in accordance with the fact that the last heat of solution is *negative* (as expressed above), *i.e.* solution of the salt in the almost saturated solution is accompanied by absorption of heat. We are led to expect this from the fact that the heat of solution changes sign from positive to negative

[1] E. von Stackelberg, *Z. physikal. Chem.*, 1896, **20**, 159; 1898, **26**, 533; Lumsden, *J. Chem. Soc.*, 1902, **81**, 350; Holsboer, *Z. physikal. Chem.*, 1902, **39**, 691; Lange and Dürr, *Z. physikal. Chem.*, 1925, **118**, 129; Campetti, *Atti R. Accad. Lincei*, 1901 [5], **10**, ii. 99. For sparingly soluble solids (non-electrolytes) one may write $d \log_e c/dT = -L/RT^2$, where L is the last heat of solution per gram-molecule; or, for electrolytes, $d \log_e c/dT = -L/iRT^2$ where i = van't Hoff's factor. See also the discussion of Braun's law, p. 164.

[2] Reicher and van Deventer, *Z. physikal. Chem.*, 1890, **5**, 559; *cf.* Ostwald, *Lehrbuch*, II., **2**, 803.

as the concentration increases; experiment also showed it to be the case.

Despite its many forms, it should be particularly noted that the solubility curve is, for any given substance, *continuous*, so long as the solid phase, or solid substance in contact with the solution, remains unchanged. If any " break " or discontinuous change in the direction of the curve occurs, it is a sign that the *solid phase has undergone alteration*. Conversely, if it is known that a change takes place in the solid phase, a break in the solubility curve can be predicted.

1. *No Solid Compounds (Hydrates) are formed.*

If, for the present, the discussion is limited to those cases where the solute forms no compound (hydrate) with the water, and where the fused solute is completely miscible with water,[1] then it follows that a break in the solubility curve must be due to a change in the crystalline form of the solid solute.

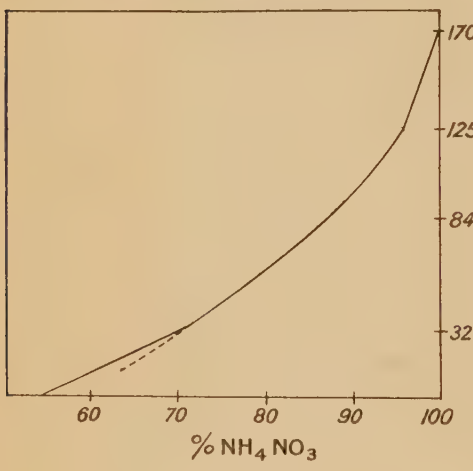


FIG. 71.

We have already learned that certain substances are capable of existing in various crystalline forms, and these forms are so related to one another that at a given temperature the relative stability of each pair of polymorphic forms undergoes change. Since each crystalline variety of a substance must have its own solubility, there must be a break in the solubility curve at the temperature of transition of the two enantiotropic forms. At this point the two solubility curves must cut, for since the two forms are in equilibrium with respect to their vapour (p. 33), they must also be in equilibrium with respect to their solutions.

The break in the solubility curve of an enantiotropic substance has been verified, more especially in the case of ammonium nitrate [2] and thallium picrate.[3]

[1] Systems in which the second component in the fused state is not completely miscible with water have already been discussed (see p. 127).

[2] Müller and Kaufmann, *Z. physikal. Chem.*, 1903, **42**, 497; Schwarz, *Beiträge zur Kenntnis der umkehrbaren Umwandlungen polymorpher Körper. Preisschrift*, Göttingen, 1892, p. 42; Millican, Joseph, and Lowry, *J. Chem. Soc.*, 1922, **121**, 959.

[3] Rabe, *Z. physikal. Chem.*, 1901, **38**, 175.

In the following table are given the values of the solubility of ammonium nitrate in water from 0° to the melting-point, 169·6° :—

Solubility of Ammonium Nitrate.

Temperature.	Solid phase.	Solubility (grams of NH_4NO_3 in 100 grams of solution).
0°	NH_4NO_3 (β-rhombic)	54·2
6·2°	,, ,,	59·70
24·5°	,, ,,	68·03
31·9°	,, ,,	71·05
34·3°	NH_4NO_3 (α-rhombic)	71·84
43·7°	,, ,,	75·71
58·4°	,, ,,	80·24
72·4°	,, ,,	84·43
83·8°	,, ,,	87·11
100·1°	NH_4NO_3 (rhombohedral)	91·10
120·8°	,, ,,	95·23
135·8°	NH_4NO_3 (regular)	97·14
157°	,, ,,	98·95
170°	,, ,,	100·0

On plotting these values, the curve shown in Fig. 71 is obtained. The curve shows distinct breaks at 32° (transition point for β- and α-rhombic) and at 125° (transition point for rhombohedral and regular or cubic). No detectible break, however, was observed at 84° (transition point for α-rhombic and rhombohedral), showing that the temperature coefficients of solubility of α-rhombic and rhombohedral ammonium nitrate are practically the same.

Suspended Transformation and Supersaturation.—As has already been learned, the transformation of the one crystalline form into the other does not necessarily take place immediately the transition point has been passed ; and it has therefore been found possible in a number of cases to follow the solubility curve of a given crystalline form beyond the point at which it ceases to be the most stable modification. Now, it will be evident from Fig. 71 that if the solubility curves for rhombohedral and regular ammonium nitrate be prolonged beyond the point of intersection, the solubility of the less stable form is greater than that of the more stable. Above 125°, for example, rhombohedral ammonium nitrate (metastable) is more soluble than regular ammonium nitrate (stable). A solution, therefore, which is saturated with respect to the less stable form, *i.e.* which is in equilibrium with that form, is *supersaturated with respect to the more stable modification*. If, therefore, a small quantity of the more stable form is introduced into the solution, the latter must deposit such an amount of the more stable form that the concentration of the solution corresponds to the solubility of the stable form at the particular temperature. Since, however, the solution is now *unsaturated* with respect to the less stable variety, the latter, if present, must pass into solution ; and

the two processes, deposition of the stable and solution of the metastable form, must go on until the latter form has entirely disappeared and a saturated solution of the stable form is obtained. There will thus be a conversion, through the medium of the solvent, of the less stable into the more stable modification. This behaviour is of practical importance in the determination of transition points (*v.* Appendix).

From the above discussion it will be seen how important is the statement of the solid phase for the definition of saturation and supersaturation.[1]

Pressure-Temperature Diagram.—Having considered the changes which occur in the concentration of the components in a solution with the temperature, we may conclude the discussion of the equilibrium between an anhydrous salt and water by studying the variation of the vapour pressure.

Since in systems of two components the two phases, solution and vapour, constitute a bivariant system, the vapour pressure is undefined, and may have different values at the same temperature, depending on the concentration. In order that there may be for each temperature a definite corresponding pressure of the vapour, a third phase must be present. This condition is satisfied by the system solid—liquid (solution)—vapour; that is, by the saturated solution (p. 165). In the case of a saturated solution, therefore, the pressure of the vapour at any given temperature is constant.

Vapour Pressure of Solid—Solution—Vapour.—It has long been known that the addition of a non-volatile solid to a liquid in which it is soluble lowers the vapour pressure of the solvent; and the diminution of the pressure is approximately proportional to the amount of substance dissolved (Law of Babo). The vapour-pressure curve, therefore, of a solution of a salt in water must lie below that for pure water. Further, in the case of a pure liquid, the vaporisation curve is a function only of the temperature (p. 15), whereas, in the case of a solution, the pressure varies both with the temperature and the *concentration*. These two factors, however, act in opposite directions; for although

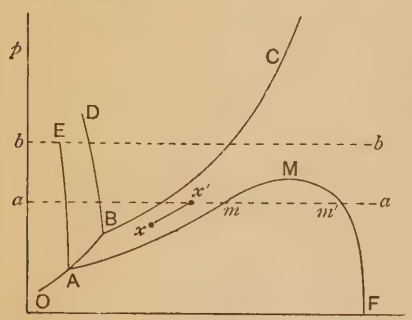


FIG. 72.

[1] With regard to the limits of supersaturation and the spontaneous crystallisation of the solute from supersaturated solutions, see Jaffé, *Z. physikal. Chem.*, 1903, **43**, 565; Miers and Isaac, *J. Chem. Soc.*, 1906, **89**, 413; 1908, **93**, 384; Hartley, Jones, and Hutchinson, *ibid.*, 825; Jones, *ibid.*, 1739; Fouquet, *Compt. rend.*, 1910, **150**, 280. For a theoretical discussion of supersaturation, see Jones and Partington, *Phil. Mag.*, 1915, **29**, 35. See also Cohen and Moesveld, *Z. physikal. Chem.*, 1920, **94**, 482.

the vapour pressure in all cases increases as the temperature rises, increase of concentration, as we have seen, lowers the vapour pressure. Again, since the concentration itself varies with the temperature, two cases have to be considered, viz. where the concentration increases with rise of temperature, and where the concentration diminishes with rise of temperature.

The relations which are found here will be best understood with the help of Fig. 72.[1] In this figure, OB represents the sublimation curve of ice, and BC the vaporisation curve of water; the curve for the solution must lie below this, and must cut the sublimation curve of ice at some temperature below the melting-point. The point of intersection A is the cryohydric point. If the solubility increases with rise of temperature, the increase of the vapour pressure due to the latter will be partially annulled. Since at first the effect of increase of temperature more than counteracts the depressing action of increase of concentration, the vapour pressure will increase on raising the temperature above the cryohydric point. If the elevation of temperature is continued, however, to the melting-point of the salt, the effect of increasing concentration makes itself more and more felt, so that the vapour-pressure curve of the solution falls more and more below that of the pure liquid, and the pressure will ultimately become equal to that of the pure salt; that is to say, practically equal to zero. The curve will therefore be of the general form AMF shown in Fig. 72. If the solubility should diminish with rise of temperature, the two factors, temperature and concentration, will act in the same direction, and the vapour-pressure curve will rise relatively more rapidly than that of the pure liquid; since, however, the pure salt is ultimately obtained, the vapour-pressure curve must in this case also finally approach the value zero.[2]

Other Univariant Systems.—Besides the univariant system salt—solution—vapour already considered, three others are possible, viz. ice—solution—vapour, ice—salt—solution, and ice—salt—vapour.

The fusion-point of a substance is lowered, as we have seen, by the addition of a foreign substance, and the depression is all the greater the larger the quantity of substance added. The vapour pressure of the water, also, is lowered by the solution in it of other substances, so that the vapour pressure of the system ice—solution—vapour must decrease as the temperature falls from the fusion-point of ice to the cryohydric point. This curve is represented by BA (Fig. 72), and is coincident with the sublimation curve of ice.

This, at first sight, strange fact will be readily understood when we consider that since ice and solution are together in equilibrium with the same vapour, they must have the same vapour pressure. For suppose

[1] Van't Hoff, *Lectures on Theoretical Chemistry*, I., p. 42; Ostwald, *Lehrbuch*, II., 2, 824. For a theoretical discussion of the curves, see Smits, *Z. physikal. Chem.*, 1911, 78, 708.

[2] It may be noted that the melting-point of the non-volatile component is not necessarily at the point of maximum temperature on the curve.

at any given temperature equilibrium to have been established in the system ice—solution—vapour, removal of the ice will not alter this equilibrium. Suppose, now, the ice and the solution placed under a bell-jar so that they have a common vapour, but are not themselves in contact; then, if they do not have the same vapour pressure, distillation must take place and the solution will become more dilute or more concentrated. Since, at the completion of this process, the ice and solution are now in equilibrium when they are not in contact, they must also be in equilibrium when they are in contact (p. 26). But if distillation has taken place the concentration of the solution must have altered, so that the ice will now be in equilibrium with a solution of a different concentration from before. But according to the Phase Rule ice cannot at one and the same temperature be in equilibrium with two solutions of different concentration, for the system ice—solution—vapour is univariant, and at any given temperature, therefore, not only the pressure but also the *concentration of the components in the solution must be constant.* Distillation could not, therefore, take place from the ice to the solution or *vice versa;* that is to say, the solution and the ice must have the same vapour pressure—the sublimation pressure of ice. The reason of the coincidence is the non-volatility of the salt: had the salt a measurable vapour pressure itself, the sublimation curve of ice and the curve for ice—solution—vapour would no longer fall together.

The curve AO represents the pressures of the system ice—salt—vapour. This curve will also be coincident with the sublimation curve of ice, on account of the non-volatility of the salt.

The equilibria of the fourth univariant system ice—salt—solution are represented by AE. Since this is a condensed system, the effect of a small change of temperature will be to cause a large change of pressure, as in the case of the fusion point of a pure substance. The direction of this curve will depend on whether there is an increase or diminution of volume on solidification; but the effect in any given case can be predicted with the help of the theorem of Le Chatelier, and calculated by means of the Clapeyron equation.

Since the cryohydric point is a quadruple point in a two-component system, it represents an invariant system. The condition of the system is, therefore, completely defined; the four phases, ice, salt, solution, vapour, can coexist only when the temperature, pressure, and concentration of the solution have constant and definite values. Addition or withdrawal of heat, therefore, can cause no alteration of the condition of the system, except a variation of the relative amounts of the phases. Addition of heat at constant volume will ultimately lead to the system salt—solution—vapour or the system ice—solution—vapour, according as ice or salt disappears first. This is readily apparent from the diagram (Fig. 72), for the systems ice—salt—solution and ice—salt—vapour can exist only at temperatures below the cryohydric point (provided the curve for ice—salt—solution slopes towards the pressure axis).

Bivariant Systems.—Besides the univariant systems already discussed, various bivariant systems are possible, the conditions for the existence of which are represented by the different areas of Fig. 72. They are as follows :—

Area.	*System.*
OAMF	Salt—vapour.
CBAMF	Solution—vapour ; salt—solution.
EABD	Salt—solution ; ice—solution.
EAO	Ice—salt.

Deliquescence.—As is evident from Fig. 72, salt can exist in contact with water vapour at pressures lower than those represented by OAMF. If, however, the pressure of the vapour is increased until it reaches a value lying on this curve at temperatures above the cryohydric point, solution will be formed ; for the curve AMF represents the equilibria between salt—solution—vapour. From this, therefore, it is clear that if the pressure of the aqueous vapour in the atmosphere is greater than that of the saturated solution of a salt, that salt will, on being placed in the air, form a solution ; it will *deliquesce*.

Separation of Salt on Evaporation.—With the help of Fig. 72 it is possible to state in a general manner whether or not salt will be deposited when a solution is evaporated under a constant pressure.[1]

The curve AMF (Fig. 72) is the vapour-pressure curve of the saturated solutions of the salt, *i.e.* it represents, as we have seen, the maximum vapour pressure at which salt can exist in contact with solution and vapour. The dotted line *aa* represents atmospheric pressure. If, now, an unsaturated solution, the composition of which is represented by the point x, is heated in an open vessel, the temperature will rise, and the vapour pressure of the solution will increase. The system will, therefore, pass along a line represented diagrammatically by xx'. At the point x' the vapour pressure of the system becomes equal to 1 atm. ; and as the vessel is open to the air, the pressure cannot further rise ; the solution boils. If the heating is continued water passes off, the concentration increases, and the boiling-point rises. The system will therefore pass along the line $x'm$, until at the point m solid salt separates out (provided supersaturation is excluded). The system is now invariant, the pressure being constant, and continued heating will no longer cause an alteration of the concentration ; as water passes off, solid salt will be deposited, and the solution will evaporate to dryness.

If, however, the atmospheric pressure is represented not by *aa* but by *bb*, then, as Fig. 72 shows, the maximum vapour pressure of the system salt—solution—vapour never reaches the pressure of 1 atm. Further, since the curve *bb* lies in the area of the bivariant system solution—vapour, there can at no point be a separation of the solid

[1] Ostwald, *Principles of Inorganic Chemistry*, translated by A. Findlay, 4th edit., p. 476 (Macmillan, 1914) ; Skirrow and Calvert, *Z. physikal. Chem.*, 1901, **37**, 217.

form ; for the system solid—solution—vapour can exist only along the curve AMF.

On evaporating the solution of a salt in an open vessel, therefore, salt can be deposited only if at some temperature the vapour pressure of the saturated solution is equal to the atmospheric pressure. This is found to be the case with most salts. In the case of aqueous solutions of sodium and potassium hydroxide, however, the vapour pressure of the saturated solution never reaches the value of 1 atm., and on evaporating these solutions therefore, in an open vessel, there is no separation of the solid. Only a homogeneous fused mass is obtained. If, however, the evaporation be carried out under a pressure which is lower than the maximum pressure of the saturated solution, separation of the solid substance will be possible.

2. *Compounds (Hydrates) are formed which Melt Incongruently.*

In the case of salts which can form crystalline hydrates which melt incongruently, the solubility curve must exhibit a break at the incongruent melting-point where the solid undergoes a change (p. 113).

Sodium Sulphate and Water.—At the ordinary temperatures, sodium sulphate crystallises from water with 10 molecules of water of crystallisation, forming Glauber's salt. On determining the solubility of this salt in water, it is found that the solubility increases as the temperature rises, the values of the solubility, represented graphically by the curve AC (Fig. 73), being given in the following table.[1] The numbers denote grams of sodium sulphate, calculated as anhydrous salt, dissolved by 100 grams of water.

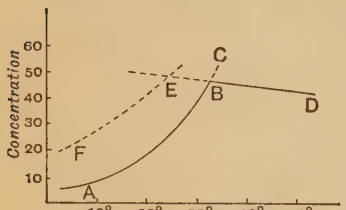


FIG. 73.

SOLUBILITY OF Na_2SO_4, $10H_2O$.

Temperature.	Solubility.
0°	5·02
10°	9·00
15°	13·20
18°	16·80
20°	19·40
25°	28·00
30°	40·00
33°	50·76
34°	55·00

[1] See Loewel, *Annales chim. phys.*, 1857 [3], **49**, 32. *Cf.* Löwenherz, *Z. physikal. Chem.*, 1895, **18**, 82 ; Lord Berkeley, *Phil. Trans.*, 1904, A, **203**, 189 ; Wuite, *Z. physikal. Chem.*, 1914, **86**, 349.

On continuing the investigation at higher temperatures, it was found that the solubility no longer increases, but *decreases with rise of temperature*. At the same time, it was observed that the solid phase is now different from that in contact with the solution at temperatures below about 33° ; for whereas in the latter case the solid phase is sodium sulphate decahydrate, at temperatures above 33° the solid phase is the anhydrous salt. The course of the solubility curve of anhydrous sodium sulphate is shown by BD, and the values of the solubility are given in the following table :—[1]

SOLUBILITY OF ANHYDROUS SODIUM SULPHATE.

Temperature.	Solubility.
18°	53·25
20°	52·76
25°	51·53
30°	50·37
33°	49·71
34°	49·53
36°	49·27
40·15°	48·78
50·40°	46·82

As is evident from the figure, the solubility curve which is obtained when anhydrous sodium sulphate is present as the solid phase, cuts the curve representing the solubility of the decahydrate, at a temperature of about 33° (see below).

If a solution of sodium sulphate which has been saturated at a temperature of about 34° be cooled down to a temperature below 17°, while care is taken that the solution is protected against access of particles of Glauber's salt, crystals of a second hydrate of sodium sulphate, having the composition $Na_2SO_4,7H_2O$, separate out. On determining the composition of the solutions in equilibrium with this hydrate at different temperatures, the following values were obtained, these values being represented by the curve FE (Fig. 73) :—

SOLUBILITY OF $Na_2SO_4,7H_2O$.

Temperature.	Solubility.
0°	19·62
10°	30·49
15°	37·43
18°	41·63
20°	44·73
25°	52·94
26°	54·97

[1] Loewel, *loc. cit.* ; Gay-Lussac, *Annales chim. phys.*, 1819, **11**, 296. For the solubility at higher temperatures, see Tilden and Shenstone, *Phil. Trans.*, 1884, **175**, 23 ; Étard, *Annales chim. phys.*, 1894 [7], **2**, 548 ; Lord Berkeley, *Phil. Trans.*, 1904, A, **203**, 189 ; Wuite, *Z. physikal. Chem.*, 1914, **86**, 349.

Since, as has already been stated, each solid substance has its own solubility curve, there are three separate curves to be considered in the case of sodium sulphate and water. Where two curves cut, the solution must be saturated with respect to two solid phases; at the point B, therefore, the point of intersection of the solubility curve of anhydrous sodium sulphate with that of the decahydrate, the solution must be saturated with respect to these two solid substances. But a system of two components existing in four phases, anhydrous salt—hydrated salt—solution—vapour, is invariant; and this invariability will remain even if only three phases are present, provided that one of the factors, pressure, temperature, or concentration of components retains a constant value. This is the case when solubilities are determined in open vessels; the pressure is then equal to atmospheric pressure. Under these circumstances, then, the system, anhydrous sodium sulphate — decahydrate—solution, will possess no degree of freedom, and can exist, therefore, only at one definite temperature and when the solution has a certain definite composition. The temperature of this point is 32·383°, or, in round figures, 32·4°,[1] and the solution contains 33·20 per cent. of anhydrous salt.

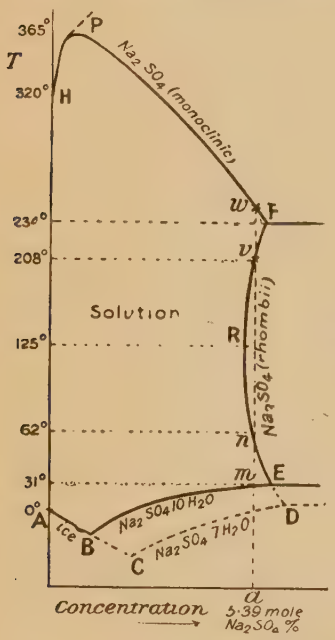


FIG. 74.

The curve showing the change of the incongruent melting-point with pressure has been determined by Tammann,[2] and has been found to pass through a point of maximum temperature.

Complete Equilibrium Diagram.—The short discussion of the solubility curves of sodium sulphate at moderate temperatures may now be supplemented by the results obtained by Wuite,[3] the complete equilibrium diagram for the system Na_2SO_4—H_2O being shown in Fig. 74. In this figure, AB

[1] Richards, *Z. physikal. Chem.*, 1898, **26**, 690; Richards and Wells, *ibid.*, 1903, **43**, 465; Dickinson and Mueller, *J. Amer. Chem. Soc.*, 1907, **29**, 1381. This temperature is not quite the same as that of the *quadruple point* anhydrous salt—hydrated salt—solution—vapour, because the latter is the temperature at which the system is under the pressure of its own vapour. Since, however, the influence of pressure on the solubility is comparatively slight (see, however, p. 165), the position of the two points will not be greatly different. The quadruple point was found by Cohen (*Z. physikal. Chem.*, 1894, **14**, 90) to be 32·6° and 30·8 mm. of mercury.

[2] *Z. physikal. Chem.*, 1903, **46**, 818.

[3] *Ibid.*, 1914, **86**, 349. See also Smits and Wuite, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 244.

is the freezing-point curve which gives the temperatures and concentrations at which ice is in equilibrium with solution.[1] At B we have a cryohydric (eutectic) point at which ice and sodium sulphate decahydrate coexist with solution. The temperature is — 1·286°, and the solution contains 4·669 grams (0·58 gram molecules) of anhydrous sodium sulphate in 100 grams of water.

The curve BE is the solubility curve for the decahydrate (p. 174), ending at the point E (32·4°), where transition to the rhombic form of anhydrous sodium sulphate occurs. The solubility curve for rhombic anhydrous sodium sulphate shows a minimum at about 125°, and ends at F (234°), the pressure at this point being 27·5 atm. Here transition of rhombic to monoclinic sodium sulphate takes place, the solubility of the latter decreasing with rise of temperature (FP). At P (365°) the critical point of the solution is reached. This coincides, practically, with the critical point of water, so that the concentration of sodium sulphate at this point may be taken as practically zero. The curve HP is the solubility curve of sodium sulphate in water vapour. This curve passes continuously into the solubility curve PF. In order that this continuity may be shown, the point P has been placed to the right of its proper place.

Suspended Transformation.—Although it is possible for the anhydrous salt to make its appearance at the temperature of the quadruple point, it will not necessarily do so; and it is therefore possible to follow the solubility curve of sodium sulphate decahydrate to a higher temperature. Since, however, the solubility of the decahydrate at temperatures above the quadruple point is greater than that of the anhydrous salt, the solution which is *saturated* with respect to the former will be *supersaturated* with respect to the latter. On bringing a small quantity of the anhydrous salt in contact with the solution, therefore, anhydrous salt will be deposited; and all the hydrated salt present will ultimately undergo conversion into the anhydrous salt, through the medium of the solution. In this case, as in all cases, the solid phase, which is the most stable at the temperature of the experiment, has at that temperature the least solubility.

Similarly, the solubility curve of anhydrous sodium sulphate has been followed to temperatures below 32·4°. Below this temperature, however, the solubility of this salt is greater than that of the decahydrate, and the saturated solution of the anhydrous salt will therefore be supersaturated for the decahydrate, and will deposit this salt if a "nucleus" is added to the solution. From this we see that at temperatures above 32·4° the anhydrous salt is the stable form, while the decahydrate is unstable (or metastable); at temperatures below 32·4° the decahydrate is stable. This temperature, therefore, is the *transition temperature* for decahydrate and anhydrous salt.

From Fig. 73 we see further that the solubility curve of the

[1] Raoult, *Z. physikal. Chem.*, 1888, **2**, 489; Loomis, *Annalen d. Physik*, 1896, **57**, 503.

anhydrous salt (which at all temperatures below 32·4° is metastable) is cut by the solubility curve of the heptahydrate; and this point of intersection (at a temperature of 24·2°) must be the *transition point* for heptahydrate and anhydrous salt. Since at all temperatures the solubility of the heptahydrate is greater than that of the decahydrate, the former hydrate must be metastable with respect to the latter; so that throughout its whole course the solubility curve of the heptahydrate represents only metastable equilibria. Sodium sulphate, therefore, forms only one stable hydrate, the decahydrate.

The solubility relations of sodium sulphate illustrate very clearly the importance of the solid phase for the definition of saturation and supersaturation. Since the solubility curve of the anhydrous salt has been followed backwards to a temperature of about 18°, it is readily seen, from Fig. 73, that at a temperature of, say, 20°, three different *saturated* solutions of sodium sulphate are possible, according as the anhydrous salt, the heptahydrate or the decahydrate, is present as the solid phase. Two of these solutions, however, would be metastable and *supersaturated with respect to the decahydrate*.

Further, the behaviour of sodium sulphate and water furnishes a very good example of the fact that a " break " in the solubility curve occurs when, and only when, the solid phase undergoes change. So long as the decahydrate, for example, remains unaltered in contact with the solution, the solubility curve is continuous; but when the anhydrous salt appears in the solid phase, a distinct change in the direction of the solubility curve is observed.

Dehydration by Means of Anhydrous Sodium Sulphate.—The change in the relative stability of sodium sulphate decahydrate and anhydrous salt in presence of water at a temperature of 32·4° explains why the latter salt cannot be employed for dehydration purposes at temperatures above the transition point. The dehydrating action of the anhydrous salt depends on the formation of the decahydrate; but since at temperatures above 32·4° the latter is unstable, and cannot be formed in presence of the anhydrous salt, this salt cannot, of course, effect a dehydration above that temperature.

Since at the incongruent melting-point (transition point) of Glauber's salt, there are three phases in equilibrium, the system will, under constant pressure (say atmospheric) be invariant. The temperature, therefore, will be perfectly definite. On this account the proposal has been made to adopt this as a fixed point in thermometry.[1] The temperature is, as we have seen, affected only comparatively slightly by change of pressure.

Pressure-Temperature Diagram.—The consideration of the pressure-temperature relations of the two components, sodium sul-

[1] Richards, *Z. physikal. Chem.*, 1898, **26**, 690. A number of other salt hydrates, having transition points ranging from 20° to 78°, which might be used for the same purpose, have been given by Richards and Churchill, *ibid.*, 1899, **28**, 313; Richards and Wells, *ibid.*, 1906, **56**, 348; Richards and Wrede, *ibid.*, 1908, **61**, 313; Richards and Fiske, *J. Amer. Chem. Soc.*, 1914, **36**, 485.

phate and water, must include not only the vapour pressure of the saturated solutions, but also that of the crystalline hydrates. The vapour pressures of salt hydrates have already been treated in a general manner (Chap. VI.), so that it is only necessary here to point out the connection between the two classes of systems.

In most cases the vapour pressure of a salt hydrate, *i.e.* the vapour pressure of the system hydrate—anhydrous salt (or lower hydrate)—vapour, is at all temperatures lower than that of the system anhydrous salt (or lower hydrate)—solution—vapour. This, however, is not a necessity; and cases are known where the vapour pressure of the former system is, under certain circumstances, equal to or higher than that of the latter. An example of this is found in sodium sulphate decahydrate.

On heating $Na_2SO_4,10H_2O$ a point is reached at which the dissociation pressure into anhydrous salt and water vapour becomes equal to the vapour pressure of the saturated solution of the anhydrous salt, as is apparent from the following measurements;[1] the differences in pressure being expressed in millimetres of a particular oil:—

Temperature . .	29·0°	30·83°	31·79°	32·09°	32·35°	32·6°
Difference of pressure	23·8	10·8	5·6	3·6	1·6	0

At 32·6°, therefore, the vapour pressures of the two systems

$Na_2SO_4,10H_2O$—Na_2SO_4—vapour,
Na_2SO_4—solution—vapour

are equal; at this temperature the four phases, $Na_2SO_4,10H_2O$; Na_2SO_4; solution; vapour, can coexist. From this it is evident that when sodium sulphate decahydrate is heated to 32·6°, the two new phases, anhydrous salt and solution, will be formed (suspended transformation being supposed excluded), and the hydrate will appear to undergo *partial fusion;* and during the process of "melting" the vapour pressure and temperature will remain constant.[2] This is, as we have seen, not a true but a so-called *incongruent* melting-point; for the composition of the liquid phase is not the same as that of the solid. It may also be regarded as the *transition point* of the equilibrium $Na_2SO_4,10H_2O \rightleftarrows Na_2SO_4 + 10H_2O$.

The vapour pressure of the different systems of sodium sulphate and water can best be studied with the help of the diagram in Fig. 75.[3] The curve ABCD represents the vapour-pressure curve of the saturated solution of anhydrous sodium sulphate. GC is the pressure curve of decahydrate + anhydrous salt, which, as we have seen, cuts the curve ABCD at the quadruple point, 32·6°. Since at this point the solution is saturated with respect to both the anhydrous salt and the deca-

[1] Van't Hoff and van Deventer, *Z. physikal. Chem.*, 1887, 1, 185. *Cf.* Cohen, *ibid.*, 1894, **14**, 88.
[2] Debray, *Compt. rend.*, 1868, **66**, 194.
[3] Van't Hoff, *Lectures on Physical Chemistry*, I., p. 67.

hydrate, the vapour-pressure curve of the saturated solution of the latter must also pass through the point C.[1] As at temperatures below this point the solubility of the decahydrate is less than that of the anhydrous salt, the vapour pressure of the solution will, in accordance with Babo's law (p. 170), be higher than that of the solution of the anhydrous salt; which was also found experimentally to be the case (curve HC).

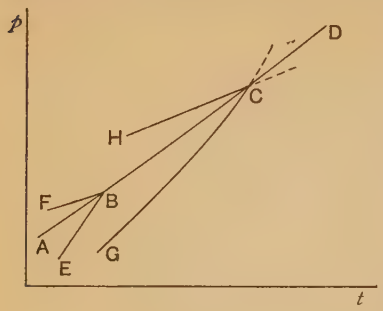


FIG. 75.

In connection with the vapour pressure of the saturated solutions of the anhydrous salt and the decahydrate, attention must be drawn to a conspicuous deviation from what was found to hold in the case of one-component systems in which a vapour phase was present (p. 40). There, it was seen that the vapour pressure of the more stable system was always *lower* than that of the less stable; in the present case, however, we find that this is no longer so. We have already learned that at temperatures below 32·6° the system decahydrate—solution—vapour is more stable than the system anhydrous salt—solution—vapour; but the vapour pressure of the latter system is, as has just been stated, lower than that of the former. At temperatures above the transition point the vapour pressure of the saturated solution of the decahydrate will be lower than that of the saturated solution of the anhydrous salt.

This behaviour depends on the fact that the less stable form is the more soluble, and that the diminution of the vapour pressure increases with the amount of salt dissolved.

With regard to sodium sulphate heptahydrate, the same considerations will hold as in the case of the decahydrate. Since at 24° the four phases heptahydrate, anhydrous salt, solution, vapour can coexist, the vapour-pressure curves of the systems hydrate—anhydrous salt—vapour (curve EB) and hydrate—solution—vapour (curve FB) must cut the pressure curve of the saturated solution of the anhydrous salt at the above temperature, as represented in Fig. 75 by the point B. This constitutes, therefore, a second quadruple point, which is, however, metastable.

From the diagram it is also evident that the dissociation pressure of the heptahydrate is higher than that of the decahydrate, although it contains less water of crystallisation. The system heptahydrate—anhydrous salt—vapour must be metastable with respect to the system decahydrate—anhydrous salt—vapour, and will pass into the latter.[2] Whether or not there is a temperature at which the vapour-pressure

[1] Cohen, *Z. physikal. Chem.*, 1894, **14**, 90.
[2] Ziz, *Schweigger's J.*, 1815, **15**, 166.

curves of the two systems intersect, and below which the heptahydrate becomes the more stable form, is not known.

Other Systems.—In the case of sodium sulphate there is only one stable hydrate. Other salts are known which exhibit a similar behaviour; and we shall therefore expect that the solubility relationships will be represented by a diagram similar to that for sodium sulphate. A considerable number of such cases have, indeed, been found,[1] and in some cases there is more than one metastable hydrate. This is found, for example, in the case of nickel iodate,[2] the solubility curves for which are given in Fig. 76. As can be seen from the figure, suspended transformation occurs, the solubility curves having in some cases been followed to a considerable distance beyond the transition point. One of the most brilliant examples, however, of suspended transformation in the case of salt hydrates, and the sluggish transition

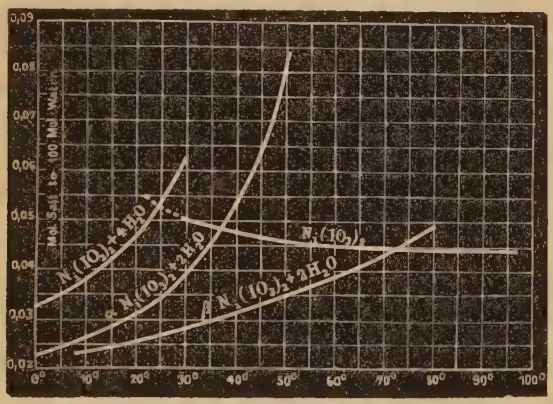


FIG. 76.

from the less stable to the more stable form, is found in the case of the hydrates of calcium chromate.[3]

In the preceding cases, the solubility curve of the hydrated salt cuts the solubility curve of the anhydrous salt. It can, however, happen that the solubility curve of one hydrate cuts the solubility curve, not of the anhydrous salt, but of a lower hydrate; in this case there will be more than one stable hydrate, each having a stable solubility curve; and these curves will intersect at the temperature of the transition point. Various examples of this behaviour are known, and we choose for illustration the solubility relationships of barium

[1] See, for example, the solubility determinations published in *Wissenschaftliche Abhandl. der physikalisch-technischen Reichsanstalt*, Vol. III., or in the *Berichte*, for the years 1897-1901.

[2] Meusser, *Ber.*, 1901, 34, 2440.

[3] Mylius and von Wrochem, *Ber.*, 1900, 33, 3693.

acetate and its hydrates.[1] In Fig. 77 the solubility is represented as ordinates and the temperatures as abscissæ.

At temperatures above 0°, barium acetate can form two stable hydrates, a trihydrate and a monohydrate. The solubility of the trihydrate increases very rapidly with rise of temperature, and has been determined up to 26·1°. At temperatures above 24·7°, however, the trihydrate is metastable with respect to the monohydrate; for at this temperature the solubility curve of the latter hydrate cuts that of the former. This is, therefore, the transition temperature for the trihydrate and monohydrate. The solubility curve of the monohydrate succeeds that of the trihydrate, and exhibits a conspicuous point of minimum solubility at about 30°. Below 24·7° the monohydrate is the less stable hydrate, but its solubility has been determined to a temperature of 22°. At 41° the solubility curve of the monohydrate

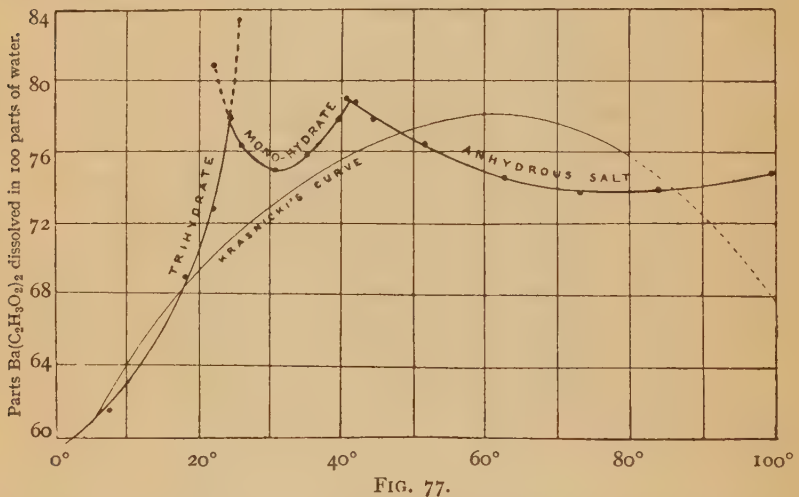


FIG. 77.

intersects that of the anhydrous salt, and this is therefore the transition temperature for the monohydrate and anhydrous salt. Above this temperature the anhydrous salt is the stable solid phase. Its solubility curve also passes through a minimum.

The diagram of solubilities of barium acetate not only illustrates the way in which the solubility curves of the different stable hydrates of a salt succeed one another, but it has also an interest and importance from another point of view. In Fig. 77 there is also shown a faintly drawn curve which is continuous throughout its whole course. This curve represents the solubility of barium acetate as determined by Krasnicki.[2] Since, however, three different solid phases can exist under the conditions of experiment, it is evident, from what has

[1] Walker and Fyffe, *J. Chem. Soc.*, 1903, **83**, 180.
[2] *Monatshefte*, 1887, **8**, 601.

already been stated (p. 168), that the different equilibria between barium acetate and water could not be represented by one *continuous curve*.

Another point which these experiments illustrate and which it is of the highest importance to bear in mind is, that in making determinations of the solubility of salts which are capable of forming hydrates, it is not only necessary to determine the composition of the solution, but *it is of equal importance to determine the composition of the solid phase in contact with it*. In view of the fact, also, that the solution equilibrium is in many cases established with comparative slowness, it is necessary to confirm the point of equilibrium, either by approaching it from higher as well as from lower temperatures, or by actually determining the rate with which the condition of equilibrium is attained. This can be accomplished by actual weighing of the dissolved salt, or by determinations of the density or of the refractive index of the solution, as well as by other methods.

3. *Compounds (Hydrates) are formed which have a Congruent Melting-point.*

In the cases which have just been considered we saw that the salt hydrates on being heated did not undergo complete fusion, but that a solid was deposited consisting of a lower hydrate or of the anhydrous salt. It has, however, long been known that certain crystalline salt hydrates (*e.g.* sodium thiosulphate, $Na_2S_2O_3,5H_2O$, sodium acetate, $NaC_2H_3O_2,3H_2O$) melt completely, and yield a liquid of the *same composition* as the crystalline salt. In the case of sodium thiosulphate pentahydrate the temperature of liquefaction is 56°; in the case of sodium acetate trihydrate, 58°. These two salts, therefore, have a definite melting-point. For the purpose of studying the behaviour of such salt hydrates, we shall choose not the substances which have just been mentioned, but two others which have been more fully studied, viz. the hydrates of calcium chloride and of ferric chloride (*cf.* p. 108).

Solubility Curve of Calcium Chloride Hexahydrate.[1] — Although calcium chloride forms several hydrates, each of which possesses its own solubility, it is nevertheless the solubility curve of the hexahydrate which will chiefly interest us at present, and we shall therefore first discuss that curve by itself.

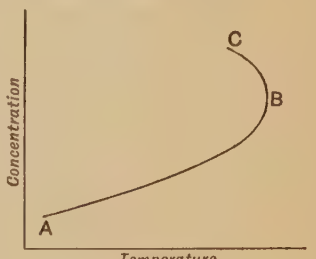


FIG. 78.

The solubility of this salt has been determined from the cryohydric (eutectic) point, which lies at about — 55°, up to the melting-point of the salt.[2] The solubility increases with rise of temperature, as is shown by the figures in the following table, and by the

[1] The equilibria between calcium chloride and water have been most completely studied by Roozeboom (*Z. physikal. Chem.*, 1889, **4**, 31).

[2] Hammerl, *Sitzungsber. Wien. Akad.*, 2te Abteil., 1878, **78**, 59; Roozeboom, *Z. physikal. Chem.*, 1889, **4**, 31;

(diagrammatic) curve AB in Fig. 78. In the table, the numbers under the heading "solubility" denote the number of grams of $CaCl_2$ dissolved in 100 grams of water; those under the heading "composition," the number of gram-molecules of water in the solution to one gram-molecule of $CaCl_2$.

Solubility of Calcium Chloride Hexahydrate.

Temperature.	Solubility.	Composition.
− 55°	42·5	14·5
− 25°	50·0	12·3
− 10°	55·0	11·2
0°	59·5	10·37
10°	65·0	9·49
20°	74·5	8·28
25°	82·0	7·52
28 5°	90·5	6·81
29·5°	95·5	6·46
30·2°	102·7	6·00
29·6°	109·0	5·70
29·2°	112·8	5·41

So far as the first portion of the curve is concerned, it resembles the most general type of solubility curve. In the present case the solubility is so great and increases so rapidly with rise of temperature, that a point is reached at which the water of crystallisation of the salt is sufficient for its complete solution. This temperature is 30·2°; and since the composition of the solution is the same as that of the solid salt, viz. 1 molecule of $CaCl_2$ to 6 molecules of water, this temperature must be the congruent melting-point of the hexahydrate. At this point, called an indifferent point (p. 110), the hydrate will fuse or the solution will solidify without change of temperature and without change of composition, when the pressure is maintained constant.

The solubility curve of calcium chloride hexahydrate, which has been drawn (as is frequently done), with temperatures as abscissæ and solubility as ordinates, differs markedly from the other solubility curves hitherto considered, in that it possesses a *retroflex portion*, represented in the figure by BC. As is evident from the figure, therefore, calcium chloride hexahydrate exhibits the peculiar and, as it was at first thought, impossible behaviour that it can be in equilibrium at one and the same temperature with two different solutions, one of which contains more, the other less, water than the solid hydrate; for it must be remembered that throughout the whole course of the curve ABC the solid phase present in equilibrium with the solution is the hexahydrate.

When, however, it is borne in mind that the so-called solubility curve is merely part of the complete equilibrium diagram, and when it is remembered that the point B represents a congruent melting-point,

the form of the curve is at once understood. One realises, in fact, that the curve shown in Fig. 78 is the counterpart of curve I., Fig. 37 (p. 109), and that the retroflex portion of the solubility curve represents the depression of the freezing-point of the compound $CaCl_2,6H_2O$ by addition of one of the components, anhydrous calcium chloride. The curve, we have seen, is continuous,[1] and its rounded form is due to a dissociation of the hexahydrate in the liquid phase (see p. 109).

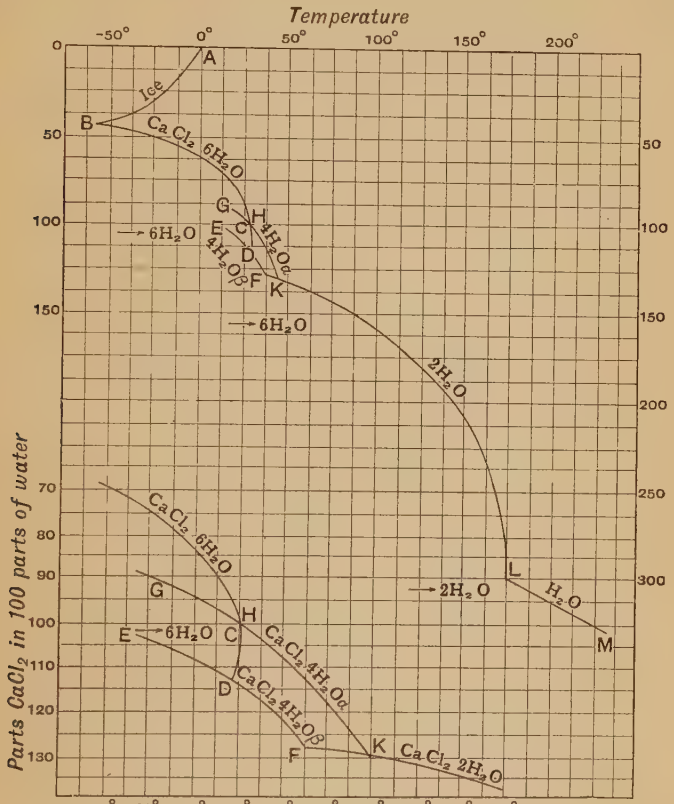


FIG. 79.

Although in taking up the discussion of the equilibria between calcium chloride and water, it was desired especially to call attention to the form of the solubility curve in the case of salt hydrates possessing a congruent melting-point, nevertheless, for the sake of completeness, brief mention may be made of the other systems which these two components can form.

[1] Lidbury, *Z. physikal. Chem.*, 1902, **39**, 453.

Besides the hexahydrate, the solubility curve of which has already been described, calcium chloride can also crystallise in two different forms, each of which contains 4 molecules of water of crystallisation; these are distinguished as α-tetrahydrate and β-tetrahydrate. Two other hydrates are also known, viz. a dihydrate and a monohydrate. The solubility curves of these different hydrates are given in Fig. 79.

On following the solubility curve of the hexahydrate from the ordinary temperature upwards, it is seen that at a temperature of 29·8° represented by the point H, it cuts the solubility curve of the α-tetrahydrate. This point, therefore, represents an invariant system in which the three phases hexahydrate, α-tetrahydrate, and solution can coexist under constant pressure. It is also the transition point for these two hydrates. Since, at temperatures above 29·8°, the α-tetrahydrate is the stable form, it is evident from the data given before (p. 184), as also from Fig. 79, that the portion of the solubility curve of the hexahydrate lying above this temperature represents *metastable* equilibria. The realisation of the metastable melting-point of the hexahydrate is, therefore, due to suspended transformation. At the transition point, 29·8°, the solubility of the hexahydrate and α-tetrahydrate is 100·6 parts of $CaCl_2$ in 100 parts of water.

The retroflex portion of the solubility curve of the hexahydrate extends to only 1° below the melting-point of the hydrate. At 29·2° crystals of a new hydrate, β-tetrahydrate, separate out, and the solution, which now contains 112·8 parts of $CaCl_2$ to 100 parts of water, is saturated with respect to the two hydrates. Throughout its whole extent the solubility curve EDF of the β-tetrahydrate represents metastable equilibria. The upper limit of the solubility curve of β-tetrahydrate is reached at 38·4° (F), the point of intersection with the curve for the dihydrate.

Above 29·8° the stable hydrate is the α-tetrahydrate; and its solubility curve extends to 45·3° (K), at which temperature it cuts the solubility curve of the dihydrate. The curve of the latter hydrate extends to 175·5° (L), and is then succeeded by the curve for the monohydrate. The solubility curve of the anhydrous salt does not begin until a temperature of about 260°. The whole diagram, therefore, shows a succession of stable hydrates, a metastable hydrate, and a metastable melting-point.

Pressure-Temperature Diagram.—The complete study of the equilibria between the two components, calcium chloride and water, would require the discussion of the vapour pressure of the different systems, and its variation with the temperature. For our present purpose, however, such a discussion would not be of great value, and will therefore be omitted here; in general, the same relationships would be found as in the case of sodium sulphate (p. 179), except that the rounded portion of the solubility curve of the hexahydrate would be represented by a similar rounded portion in the pressure curve.[1]

[1] See Roozeboom, *Z. physikal. Chem.*, 1889, **4**, 31.

As in the case of sodium sulphate, the transition points of the different hydrates would be indicated by breaks in the curve of pressures. Finally, mention may again be made of the difference of the pressure of dissociation of the hexahydrate according as it becomes dehydrated to the α- or the β-tetrahydrate (p. 186).

The Hydrates of Ferric Chloride.—A better illustration of the formation of compounds possessing a congruent melting-point is afforded by the hydrates of ferric chloride, which not only possess definite points of fusion but these melting-points are stable. A very brief description of the relations met with will suffice.[1]

Ferric chloride can form no less than four stable hydrates, viz. $Fe_2Cl_6,12H_2O$, $Fe_2Cl_6,7H_2O$, $Fe_2Cl_6,5H_2O$, and $Fe_2Cl_6,4H_2O$, and each of these hydrates possesses a congruent stable melting-point. On the basis of the discussion given on page 186, therefore, we shall expect

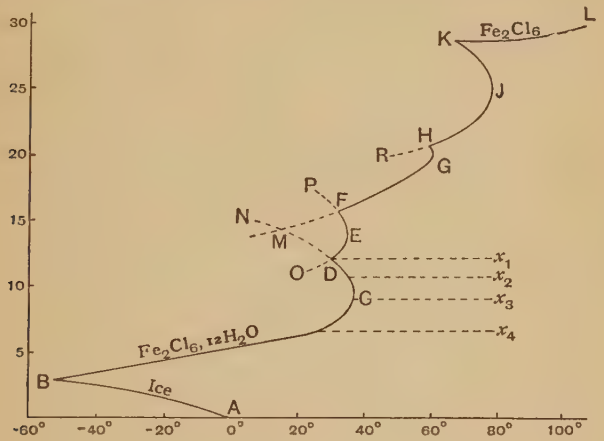


FIG. 80.

that the solubility (equilibrium) curves of these different hydrates will exhibit a series of *temperature maxima ;* the points of maximum temperature representing systems in which the composition of the solid and liquid phases is the same. A graphical representation of the solubility relations is given in Fig. 80, and the composition of the different saturated solutions which can be formed is given in the tables on the next page, the composition being expressed in molecules of Fe_2Cl_6 to 100 molecules of water. The figures printed in thick type refer to transition and melting-points.

The lowest portion of the curve, AB, represents the equilibria between ice and solutions containing ferric chloride. It represents,

[1] Roozeboom, *Z. physikal. Chem.*, 1892, **10**, 477. The formula of ferric chloride has been doubled, in order to avoid fractions in the expression of the water of crystallisation.

in other words, the lowering of the freezing-point of water by addition of ferric chloride. At the point B (— 55°), the cryohydric (eutectic) point is reached, at which the solution is in equilibrium with ice and ferric chloride dodecahydrate. As has already been shown, such a point represents an invariant system, the pressure being constant, equal to atmospheric pressure; and the liquid phase will, therefore, solidify to a mixture of ice and hydrate without change of temperature. If heat is added, ice will melt and the system will pass to the curve BCDN, which is the solubility curve of the dodecahydrate. At C (37°), the point of maximum temperature, the hydrate melts completely. The retroflex portion of this curve can be followed backwards to a temperature of 8°, but below 27·4° (D), the solutions are supersaturated

COMPOSITION OF THE SATURATED SOLUTIONS OF FERRIC CHLORIDE AND ITS HYDRATES.

(*The name placed at the head of each table is the solid phase.*)

Ice.		Fe_2Cl_6, $12H_2O$.		Fe_2Cl_6, $7H_2O$.	
Temperature.	Composition.	Temperature.	Composition.	Temperature.	Composition.
— 55°	± 2·75	— 55°	± 2·75	20°	11·35
— 40°	2·37	— 41°	2·81	**27·4°**	**12·15**
— 27·5°	1·90	— 27°	2·98	32°	13·55
— 20·5°	1·64	0°	4·13	**32·5°**	**14·29**
— 10°	1·00	10°	4·54	30°	**15·12**
0°	0	20°	5·10	25°	15·54
		30°	5·93		
		35°	6·78		
		36·5°	7·93		
		37°	**8·33**		
		36°	9·29		
		33°	10·45		
		30°	11·20		
		27·4°	**12·15**		
		20°	12·83		
		10°	13·20		
Fe_2Cl_6, $5H_2O$.		8°	13·70	Fe_2Cl_6, $4H_2O$.	
Temperature.	Composition.	Fe_2Cl_6 (ANHYDROUS).		Temperature.	Composition.
12°	12·87			50°	19·96
20°	13·95	Temperature.	Composition.	**55°**	**20·32**
27°	14·85			60°	20·70
30°	**15·12**			69°	21·53
35°	15·64	**66°**	**29·20**	72·5°	23·35
50°	17·50	70°	29·42	**73·5°**	**25·00**
55°	19·15	75°	28·92	72·5°	26·15
56°	**20·00**	80°	29·20	70°	27·90
55°	**20·32**	100°	29·75	**66°**	**29·20**

with respect to the heptahydrate; point D is the eutectic point for dodecahydrate and heptahydrate. The curve DEF is the solubility curve of the heptahydrate, E being the melting-point, 32·5°. On further increasing the quantity of ferric chloride, the temperature of equilibrium is lowered until at F (30°) another eutectic point is reached, at which the heptahydrate and pentahydrate can coexist with solution. Then follow the solubility curves for the pentahydrate, the tetrahydrate, and the anhydrous salt; G (56°) is the melting-point of the former hydrate, J (73·5°) the melting-point of the latter. H and K, the points at which the curves intersect, represent eutectic points; the temperature of the former is 55°, that of the latter 66°. The dotted portions of the curves represent metastable equilibria.

As is seen from the diagram, a remarkable series of solubility curves is obtained, each passing through a point of maximum temperature, the whole series of curves forming a "festoon." To the right of the series of curves the diagram represents unsaturated solutions; to the left, supersaturated.

If an unsaturated solution, the composition of which is represented by a point in the field to the right of the solubility curves, is cooled down, the result obtained will differ according as the composition of the solution is the same as that of a cryohydric point, or of a melting-point, or has an intermediate value. Thus, if a solution represented by x_1 is cooled down, the composition will remain unchanged as indicated by the horizontal dotted line, until the point D is reached. At this point, dodecahydrate and heptahydrate will separate out, and the liquid will ultimately solidify completely to a mixture or "conglomerate" of these two hydrates; the temperature of the system remaining constant until complete solidification has taken place. If, on the other hand, a solution of the composition x_3 is cooled down, ferric chloride dodecahydrate will be formed when the temperature has fallen to that represented by C, and the solution will completely solidify, without alteration of temperature, with formation of this hydrate. In both these cases, therefore, a point is reached at which complete solidification occurs without change of temperature.

Somewhat different, however, is the result when the solution has an intermediate composition, as represented by x_2 or x_4. In the former case the dodecahydrate will first of all separate out, but on further withdrawal of heat the temperature will fall, the solution will become relatively richer in ferric chloride, owing to separation of the hydrate, and ultimately the eutectic point D will be reached, at which complete solidification will occur. Similarly with the second solution. Ferric chloride dodecahydrate will first be formed, and the temperature will gradually fall, the composition of the solution following the curve CB until the cryohydric point B is reached, when the whole will solidify to a conglomerate of ice and dodecahydrate.

Suspended Transformation.—Not only can the upper branch of the solubility curve of the dodecahydrate be followed backwards to a temperature of 8°, or about 19° below the temperature of transition to

the heptahydrate, but suspended transformation has also been observed in the case of the heptahydrate and the pentahydrate. To such an extent is this the case that the solubility curve of the latter hydrate has been followed downwards to its point of intersection with the curve for the dodecahydrate. This point of intersection, represented in Fig. 80 by M, lies at a temperature of about 15°; and at this temperature, therefore, it is possible for the two solid phases, dodecahydrate and pentahydrate, to coexist, so that M is a eutectic point for the dodecahydrate and the pentahydrate. It is, however, a metastable eutectic point, for it lies in the region of supersaturation with respect to the heptahydrate; and it can be realised only because of the fact that the latter hydrate is not readily formed.

Evaporation of Solutions at Constant Temperature.—On evaporating dilute solutions of ferric chloride at constant temperature, a remarkable series of changes is observed, which, however, will be understood with the help of Fig. 81. Suppose an unsaturated solution, the composition of which is represented by the point x_1, is evaporated at a temperature of about 17°-18°. As water passes off, the composition of the solution will follow the dotted line of constant temperature, until at the point where it cuts the curve BC the solid hydrate $Fe_2Cl_6,12H_2O$ separates out. As water continues to be removed, the hydrate must be deposited (in order that the solution shall remain saturated), until finally the solution dries up to the hydrate. As dehydration proceeds, the heptahydrate can be formed, and the dodecahydrate will finally pass into the heptahydrate; and this, in turn, into the pentahydrate.

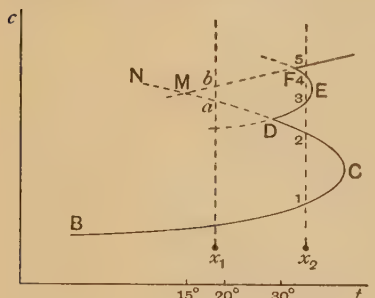


FIG. 81.

But the heptahydrate is not always formed by the dehydration of the dodecahydrate, and the behaviour on evaporation is therefore somewhat perplexing at first sight. After the solution has dried to the dodecahydrate, as explained above, further removal of water causes liquefaction, and the system is now represented by the point of intersection at *a*; at this point the solid hydrate is in equilibrium with a solution containing relatively more ferric chloride. If, therefore, evaporation is continued, the solid hydrate must *pass into solution* in order that the composition of the latter may remain unchanged, so that ultimately a liquid will again be obtained. A very slight further dehydration will bring the solution into the state represented by *b*, at which the pentahydrate is formed, and the solution will at last disappear and leave this hydrate alone.

Without the information to be obtained from the curves in Figs. 80 and 81, the phenomena which would be observed on carrying out the

evaporation at a temperature of about 31°-32° would be still more bewildering. The composition of the different solutions formed will be represented by the perpendicular line $x_2$12345. Evaporation will first cause the separation of the dodecahydrate, and then total disappearance of the liquid phase. Then liquefaction will occur, and the system will now be represented by the point 2, in which condition it will remain until the solid hydrate has disappeared. Following this there will be deposition of the heptahydrate (point 3), with subsequent disappearance of the liquid phase. Further dehydration will again cause liquefaction, when the concentration of the solution will be represented by the point 4; the heptahydrate will ultimately disappear, and then will ensue the deposition of the pentahydrate, and complete solidification will result. On evaporating a solution, therefore, of the composition x_2, the following series of phenomena will be observed: solidification to dodecahydrate; liquefaction; solidification to heptahydrate; liquefaction; solidification to pentahydrate.[1]

Although ferric chloride and water form the largest and best-studied series of hydrates possessing congruent melting-points, examples of similar hydrates are not few in number; and more careful investigation is constantly adding to the list.[2] In all these cases the solubility curve will show a point of maximum temperature, at which the hydrate melts, and will end, above and below, in a cryohydric point. Conversely, if such a curve is found in a system of two components, we can argue that a definite compound of the components possessing a congruent melting-point is formed.

Inevaporable Solutions.—If a saturated solution in contact with two hydrates, or with a hydrate and anhydrous salt is heated, the temperature and composition of the solution will, of course, remain unchanged so long as the two solid phases are present, for such a system is invariant. In addition to this, however, the *quantity* of the solution will also remain unchanged, the water which evaporates being supplied by the higher hydrate. The same phenomenon is also observed in the case of cryohydric points when ice is a solid phase; so long as the latter is present, evaporation will be accompanied by fusion of the ice, and the quantity of solution will remain constant. Such solutions are called *inevaporable.*[3]

Potassium Iodide and Sulphur Dioxide.—In order still further to illustrate the application of the principles of the Phase Rule to the study of systems formed by a volatile and a non-volatile component, a brief description may be given of the behaviour of sulphur dioxide and potassium iodide. After it had been found [4] that liquid sulphur dioxide has the property of dissolving potassium iodide, and that the solutions thus obtained present certain peculiarities of behaviour, the question arose as to whether or not compounds are formed between

[1] Roozeboom, *Z. physikal. Chem.*, 1892, **10**, 477.

[2] A similar series of hydrates is formed by zinc chloride and water (Dietz and Mylius, *Z. anorgan. Chem.*, 1905, **44**, 209).

[3] Meyerhoffer, *Ber.*, 1897, **30**, 1810.

[4] Walden, *Ber.*, 1899, **32**, 2863.

the sulphur dioxide and the potassium iodide, and if so, what these compounds are. To find an answer to this question, Walden and Centnerszwer [1] made a complete investigation of the solubility curves (equilibrium curves) of these two components, the investigation extending from the freezing-point to the critical point of sulphur dioxide. For convenience of reference, the results which they obtained are represented diagrammatically in Fig. 82. The freezing-point (A) of pure sulphur dioxide was found to be — 72·7°. Addition of potassium iodide lowered the freezing-point, but the maximum depression obtained was very small, and was reached when the concentration of the potassium iodide in the solution was only 0·336 mols. per cent. Beyond this point, an increase in the concentration of the iodide was accompanied by an elevation of the freezing-point, the change of the freezing-point with the concentration being represented by the curve BC. The solid which separated from the solutions represented by BC was a bright *yellow* crystalline substance. At the point C (— 23·4°) a temperature-maximum was reached; and as the concentration of the potassium iodide was continuously increased, the temperature of

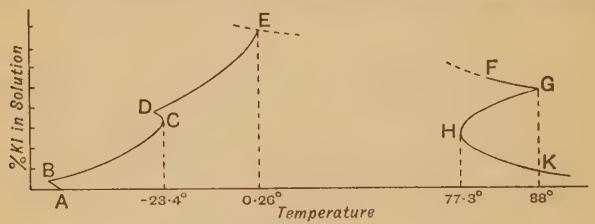


Fig. 82.

equilibrium first fell and then slowly rose, until at + 0·26° (E) a second temperature-maximum was registered. On passing the point D, the solid which was deposited from the solution was a *red* crystalline substance. On withdrawing sulphur dioxide from the system, the solution became turbid, and the temperature remained constant. The investigation was not pursued further at this point, the attention being then directed to the equilibria at higher temperatures.

When a solution of potassium iodide in liquid sulphur dioxide containing 1·49 per cent. of potassium iodide was heated, solid (potassium iodide) was deposited at a temperature of 96·4°. Solutions containing more than about 3 per cent. of the iodide separated, on being heated, into two layers, and the temperature at which the liquid became heterogeneous fell as the concentration was increased; a temperature-minimum being obtained with solutions containing 12 per cent. of potassium iodide. On the other hand, solutions containing 30·9 per cent. of the iodide, on being heated, deposited potassium iodide; while a solution containing 24·5 per cent. of the salt first separated into two layers at

[1] *Z. physikal. Chem.*, 1903, **42**, 432.

89·3°, and then, on cooling, solid was deposited and one of the liquid layers disappeared.

Such are, in brief, the results of experiment; their interpretation in the light of the Phase Rule is the following:—

The curve AB is the freezing-point curve of solid sulphur dioxide in contact with solutions of potassium iodide. BCD is the solubility curve of the *yellow* crystalline solid which is deposited from the solutions. C, the temperature-maximum, is the melting-point of this yellow solid, and the composition of the latter must be the same as that of the solution at this point (p. 184), which was found to be that represented by the formula $KI,14SO_2$. B is therefore the eutectic point, at which solid sulphur dioxide and the compound $KI,14SO_2$ can exist together in equilibrium with solution and vapour. The curve DE is the solubility curve of the *red* crystalline solid, and the point E, at which the composition of solution and solid is the same, is the melting-point of the solid. The composition of this substance was found to be $KI,4SO_2$.[1] D is, therefore, the eutectic point at which the compounds $KI,14SO_2$ and $KI,4SO_2$ can co-exist in equilibrium with solution and vapour. The curve DE does not exhibit a retroflex portion; on the contrary, on attempting to obtain more concentrated solutions in equilibrium with the compound $KI,4SO_2$, a new solid phase (probably potassium iodide) was formed. Since at this point there are four phases in equilibrium, viz. the compound $KI,4SO_2$, potassium iodide, solution, and vapour, the system is invariant. E is, therefore, the *transition point* for $KI,4SO_2$ and KI.

Passing to higher temperatures, FG is the solubility curve of potassium iodide in sulphur dioxide; at G two liquid phases are formed, and the system therefore becomes invariant (*cf.* p. 128). The curve GHK is the solubility curve for two partially miscible liquids; and since complete miscibility occurs on *lowering* the temperature, the curve is similar to that obtained with triethylamine and water (p. 93). K is also an invariant point at which potassium iodide is in equilibrium with two liquid phases and vapour.

Point.	Temperature.	Composition of the solution per cent. KI.
A (m.p. of SO_2)	− 72·7°	—
B (eutectic point)	—	0·86
C (m.p. of $KI,14SO_2$)	− 23·4°	17·63
E (m.p. of $KI,4SO_2$)	+ 0·26°	39·33
G (KI + two liquid phases)	(about) 88°	24·0
H (critical solution point)	77·3°	12
K (KI + two liquid phases)	(about) 88°	2·7

[1] This composition was also confirmed by measurements of the vapour pressure (*cf.* p. 85).

The complete investigation of the equilibria between sulphur dioxide and potassium iodide, therefore, shows that these two components form the compounds $KI,14SO_2$ and $KI,4SO_2$; and that when solutions having a concentration between those represented by the points G and K are heated, separation into two layers occurs. The temperatures and concentrations of the different characteristic points are as shown in above table.

II. Both Components are Volatile.

General.—In the preceding pages certain restrictions were imposed on the discussion of the equilibria between two components; but in the present section the restriction that only one of the components is volatile will be allowed to fall, and the general behaviour of two volatile[1] components, each of which is capable of forming a liquid solution with the other, will be studied. As we shall see, however, the removal of the previous restriction produces no alteration in the general aspect of the equilibrium curves for concentration and temperature, but changes to some extent the appearance of the pressure - temperature diagram. The latter would become still more complicated if account were taken not only of the total pressure but also of the partial pressures of the two components in the vapour phase; this complication, however, will not be introduced into the present discussion.[2] In this chapter we shall consider the systems formed by the two components iodine and chlorine, and sulphur dioxide and water.

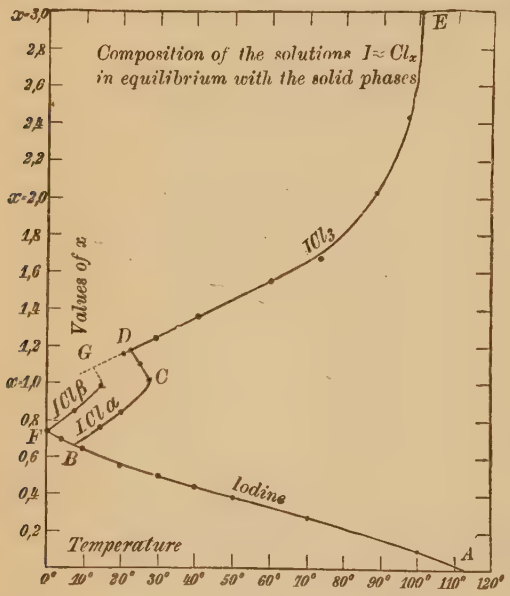


Fig. 83.

[1] Since all substances are no doubt volatile to a certain extent at some temperature, it is to be understood here that the substances are appreciably volatile at the temperature of the experiment.

[2] For a general discussion of the partial pressures in a system of two components see Bancroft, *J. Physical Chem.*, 1899, **3**, 1.

A. **Iodine and Chlorine.**—The different systems furnished by iodine and chlorine, rendered classical by the studies of Stortenbeker,[1] form a very complete example of equilibria in a two-component system. We shall first of all consider the relations between concentration and temperature, with the help of the accompanying diagram, Fig. 83.

Concentration-Temperature Diagram.—In this diagram the temperatures are taken as the abscissæ, and the composition of the solution, expressed in atoms of chlorine to one atom of iodine,[2] is represented by the ordinates. In the diagram, A represents the melting-point of pure iodine, 114°. If chlorine is added to the system, a solution of chlorine in liquid iodine is obtained, and the temperature at which solid iodine is in equilibrium with the liquid solution will be all the lower the greater the concentration of the chlorine. We therefore obtain the curve ABF, which represents the composition of the solution with which solid iodine is in equilibrium at different temperatures. This curve can be followed down to 0°, but at temperatures below 7·9° (B) it represents metastable equilibria. At B iodine monochloride can be formed, and if present the system becomes invariant; B is therefore a quadruple point at which the four phases, iodine, iodine monochloride, solution, and vapour, can co-exist. Continued withdrawal of heat at this point will therefore lead to the complete solidification of the solution to a mixture or conglomerate of iodine and iodine monochloride, while the temperature remains constant during the process. B is the eutectic point for iodine and iodine monochloride.

Just as we found in the case of aqueous salt solutions that at temperatures above the cryohydric or eutectic point, two different solutions could exist, one in equilibrium with ice, the other in equilibrium with the salt (or salt hydrate), so in the case of iodine and chlorine there can be two solutions above the eutectic point B, one containing a lower proportion of chlorine in equilibrium with iodine, the other containing a higher proportion of chlorine in equilibrium with iodine monochloride. The composition of the latter solution is represented by the curve BCD. As the concentration of chlorine is increased, the temperature at which there is equilibrium between iodine monochloride and solution rises until a point is reached at which the composition of the solution is the same as that of the solid. At this point (C), iodine monochloride melts. Addition of one of the components will lower the temperature of fusion, and a continuous curve,[3] exhibitng a temperature maximum, will be obtained. At temperatures below its

[1] *Z. physikal. Chem.*, 1889, **3**, 11; *Rec. trav. chim. Pays-Bas*, 1888, **7**, 152.

[2] The composition of a solution is represented symbolically by placing a double wavy line between the symbols of the components, and indicating the number of atoms present in the ordinary manner: thus, $I\!\sim\!\sim\!Cl_x$ represents a solution containing x atoms of chlorine to one atom of iodine (Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 450).

[3] Since iodine monochloride in the liquid state is only very slightly dissociated, the bend at C is very sharp (see p. 109). See also the investigation of the system pyridine and methyl iodide (Aten, *Z. physikal. Chem.*, 1906, **54**, 124).

melting-point, therefore, iodine monochloride can be in equilibrium with two different solutions.

The upper portion of this curve, CD, can be followed downwards to a temperature of 22·7°. At this temperature iodine trichloride can separate out, and a second quadruple point (D) is obtained. This is the eutectic point for iodine monochloride and iodine trichloride.

By addition of heat and increase in the amount of chlorine, the iodine monochloride disappears, and the system passes along the curve DE, which represents the composition of the solutions in equilibrium with solid iodine trichloride. The concentration of chlorine in the solution increases as the temperature is raised, until at the point E, where the solution has the same composition as the solid, the maximum temperature is reached; the iodine trichloride melts. On increasing still further the concentration of chlorine in the solution, the temperature of equilibrium falls, and a continuous curve, similar to that for the monochloride, is obtained. The upper branch of this curve has been followed down to a temperature of 30°, the solution at this point containing 99·6 per cent. of chlorine.[1] The very rounded form of the curve is due to the trichloride being largely dissociated in the liquid state.

One curve still remains to be considered. As has already been mentioned, iodine monochloride can exist in two crystalline forms, only one of which, however, is stable at temperatures below the melting-point; the two forms are *monotropic* (p. 35). The stable form which melts at 27·2° is called the α form, while the less stable variety, melting at 13·9°, is known as the β form. If the presence of α-ICl is excluded, it is possible to obtain the β form, and to study the conditions of equilibrium between it and solutions of iodine and chlorine, from the eutectic point F to the melting-point G. As the β-ICl becomes less stable in presence of excess of chlorine, it has not been possible to study the portion of the curve represented by the dotted continuation of FG.

The following table gives some of the numerical data from which Fig. 83 was constructed :—[2]

IODINE AND CHLORINE.

I. *Invariant Systems.*

Temperature.	Pressure.	Phases present.		
		Solid.	Liquid.	Vapour.
7·9°	11 mm.	I_2, α-ICl	I≈≈≈$Cl_{0\cdot66}$	$I + Cl_{0\cdot92}$
0·9°	—	I_2, β-ICl	I≈≈≈$Cl_{0\cdot72}$	—
22·7°	42 mm.	α-ICl, ICl_3	I≈≈≈$Cl_{1\cdot19}$	$I + Cl_{1\cdot75}$
[− 102°	< 1 atm.	ICl_3, Cl_2	I≈≈≈Cl	$I + Cl_n$]

[1] This upper branch of the curve is not shown in the figure, as the ordinate corresponding to 30° would be very great.

[2] Stortenbeker, *Z. physikal. Chem.*, 1889, **3**, 22.

II. *Melting-points.*

A. Iodine,[1] 114·15° (pressure, 89·8 mm.).
C. α-Iodine monochloride, 27·2° (pressure, 37 mm.).
E. Iodine trichloride, 101° (pressure, 16 atm.).
G. β-Iodine monochloride, 13·9°.

Since the vapour pressure at the melting-point of iodine trichloride amounts to 16 atm., the experiments must of course be carried out in closed vessels. At 63·7° the vapour pressure of the system trichloride —solution—vapour is equal to 1 atm.

Pressure-Temperature Diagram.—In this diagram there are represented the values of the vapour pressure of the saturated solutions of chlorine and iodine. To give a complete picture of the relations between pressure, temperature, and concentration, a solid model would be required, with three axes at right angles to one another along which could be measured the values of pressure, temperature, and concentration of the components in the solution. Instead of this, however, there may be employed the accompanying projection figure [2] (Fig. 84), the lower portion of which shows the projection of the equilibrium curve on the surface containing the concentration and temperature axes, while the upper portion is the projection on the plane containing the pressure and temperature axes. The lower portion is therefore a concentration-temperature diagram; the upper portion, a pressure-temperature diagram. The corresponding points of the two diagrams are joined by dotted lines.

Corresponding to the point C, the melting-point of pure iodine, there is the point C′, which represents the vapour pressure of iodine at its melting-point. At this point three curves cut: 1, the sublimation curve of iodine; 2, the vaporisation curve of fused iodine; 3, C_1B_1, the vapour-pressure curve of the saturated solutions in equilibrium with solid iodine. Starting, therefore, with the system solid iodine—liquid iodine, addition of chlorine will cause the temperature of equilibrium to fall continuously, while the vapour pressure will first increase, pass through a maximum and then fall continuously until the eutectic point, B (B_1), is reached.[3] At this point the system is invariant, and the pressure will therefore remain constant until all the iodine has disappeared. As the concentration of the chlorine increases in the manner represented by the curve BfH, the pressure of the vapour also increases as represented by the curve $B_1f_1H_1$. At H_1, the eutectic point for iodine monochloride and iodine trichloride, the pressure again remains constant until all the monochloride has disappeared. As the concentration of the solution passes along the curve HF, the pressure

[1] Ramsay and Young, *J. Chem. Soc.*, 1886, **49**, 458.
[2] Van't Hoff, *Lectures on Physical Chemistry*, I., p. 77 (Arnold).
[3] This is different from what we found in the case of non-volatile solutes (p. 170). In the present case the *partial pressure* of the iodine in the vapour will be lowered by addition of chlorine, but the *total pressure* is increased.

of the vapour increases as represented by the curve H_1F_1; F_1 represents the pressure of the vapour at the melting-point of iodine trichloride. If the concentration of the chlorine in the solution is continuously increased from this point, the vapour pressure first increases and then decreases, until the eutectic point for iodine trichloride and solid chlorine is reached (D_1). Curves Cl_2—solid and Cl_2—liquid represent the sublimation and vaporisation curves of chlorine, the melting-point of chlorine being — 102°.

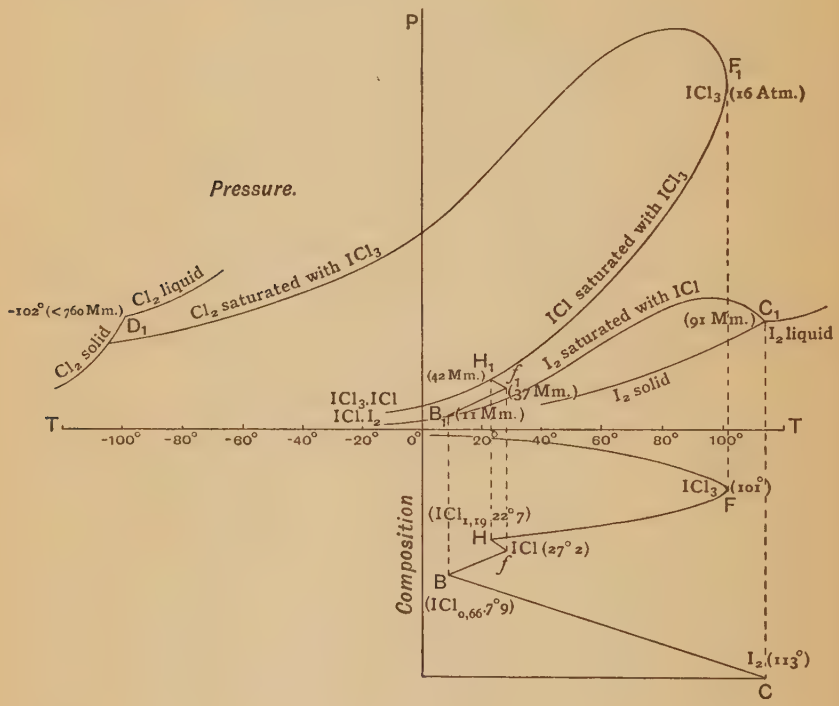


FIG. 84

Although complete measurements of the vapour pressure of the different systems of pure iodine to pure chlorine have not been made, the experimental data are nevertheless sufficient to allow of the general form of the curves being indicated with certainty.

Bivariant Systems.—To these, only a brief reference need be made. Since there are two components, two phases will form a bivariant system. The fields in which these systems can exist are shown in Fig. 84 and Fig. 85, which is a more diagrammatic representation of a portion of Fig. 84.

I. Iodine—vapour.
II. Solution—vapour.
III. Iodine trichloride—vapour.
IV. Iodine monochloride—vapour.

The conditions for the existence of these systems will probably be best understood from Fig. 85. Since the curve B′A′ represents the pressures under which the system iodine—solution—vapour can exist, increase of volume (diminution of pressure) will cause the volatilisation of the solution, and the system iodine—vapour will remain. If, therefore, we start with a system represented by *a*, diminution of pressure at constant temperature will lead to the condition represented by *x*. On the other hand, increase of pressure at *a* will lead to the condensation of a portion of the vapour phase. Since the concentration of chlorine in the vapour is greater than in the solution, condensation of vapour would increase the concentration of chlorine in the solution ; a certain amount of iodine must therefore pass into solution in order that the composition of the latter shall remain unchanged.[1] If, therefore, the volume of vapour be sufficiently great, continued diminution of volume will ultimately lead to the disappearance of all the iodine, and there will remain only solution and vapour (field II.). As the diminution of volume is continued, the vapour pressure and the concentration of the chlorine in the solution will increase, until, when the pressure has reached the value *b*, iodine monochloride can separate out. The system, therefore, again becomes univariant, and at constant temperature the pressure and composition of the phases must remain unchanged. Diminution of volume will therefore not effect an increase of pressure, but a condensation of the vapour ; and since this is richer in chlorine than the solution, solid iodine monochloride must separate out in order that the concentration of the solution remain unchanged.[2] As the result, therefore, we obtain the bivariant system iodine monochloride—vapour.

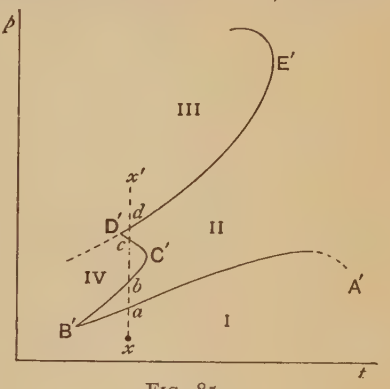


FIG. 85.

A detailed discussion of the effect of a continued increase of pressure will not be necessary. From what has already been said, and with the help of Fig. 85, it will readily be understood that this will lead

[1] The diminution of volume is supposed to be carried out at constant temperature. The pressure and the composition of the phases must, therefore, remain unchanged, and only the relative amounts of these can undergo alteration.

[2] At point *b* the ratio of chlorine to iodine in the solution is less than in the monochloride, so that by the separation of this the excess of chlorine yielded by the condensation of the vapour is removed.

successively to the univariant system (*c*), iodine monochloride—solution—vapour; the bivariant system solution—vapour (field II.); the univariant system (*d*), iodine trichloride—solution—vapour; and the bivariant system *x'*, iodine trichloride—vapour. If the temperature of the experiment is above the melting-point of the monochloride, then the systems in which this compound occurs will not be formed.

B. **Sulphur Dioxide and Water.**—In the case just studied we have seen that the components can combine to form definite compounds possessing stable melting-points. The curves of equilibrium, therefore, resemble in their general aspect those of calcium chloride and water, or of ferric chloride and water. In the case of sulphur dioxide and water, however, the melting-point of the compound formed cannot be realised, because transition to another system occurs; retroflex concentration-temperature curves are therefore not found here, but the curves exhibit breaks or sudden changes in direction at the transition points, as in the case of the systems formed by sodium sulphate and water. The case of sulphur dioxide and water is also of interest from the fact that two liquid phases can be formed.

The phases which occur are—Solid: ice, sulphur dioxide hydrate, $SO_2,7H_2O$. Liquid: two solutions, the one containing excess of sulphur dioxide, the other excess of water, and represented by the symbols $SO_2 \approx\approx x H_2O$ (solution I.), and $H_2O \approx\approx y SO_2$ (solution II.). Vapour: a mixture of sulphur dioxide and water vapour in varying proportions. Since there are two components, sulphur dioxide and water, the number of possible systems is considerable. Only the following, however, have been studied:—

I. *Invariant Systems: Four co-existing phases.*
   (*a*) Ice, hydrate, solution, vapour.
   (*b*) Hydrate, solution I., solution II., vapour.

II. *Univariant Systems: Three co-existing phases.*
   (*a*) Hydrate, solution I., vapour.
   (*b*) Hydrate, solution II., vapour.
   (*c*) Solution I., solution II., vapour.
   (*d*) Hydrate, solution I., solution II.
   (*e*) Hydrate, ice, vapour.
   (*f*) Ice, solution II., vapour.
   (*g*) Ice, hydrate, solution II.

III. *Bivariant Systems: Two co-existing phases.*
   (*a*) Hydrate, solution I.
   (*b*) Hydrate, solution II.
   (*c*) Hydrate, vapour.
   (*d*) Hydrate, ice.
   (*e*) Solution I., solution II.
   (*f*) Solution I., vapour.
   (*g*) Solution I., ice.
   (*h*) Solution II., vapour.
   (*i*) Solution II., ice.
   (*j*) Ice, vapour.

Pressure-Temperature Diagram.[1]—If sulphur dioxide is passed into water at 0°, a solution will be formed and the temperature at which ice can exist in equilibrium with this solution will fall more and more as the concentration of the sulphur dioxide increases. At — 2·6°, however, an eutectic point is reached at which solid hydrate separates out, and the system becomes invariant. The curve AB (Fig. 86), therefore, represents the pressure of the system ice—solution II.—vapour, and B represents the temperature and pressure at which the invariant system ice—hydrate—solution II.—vapour can exist. At this point the temperature is — 2·6°, and the pressure 21·2 cm. If heat is withdrawn from this system, the solution will ultimately solidify to a mixture of ice and hydrate, and there will be obtained the univariant system ice—hydrate—vapour. The vapour pressure of this system has been determined down to a temperature of — 9·5°, at which temperature the pressure amounts to 15 cm. The pressures for this system are represented by the curve BC. If at the point B the volume is diminished, the pressure must remain constant, but the relative amounts of the different phases will undergo change. If suitable quantities of these are present, diminution of volume will ultimately lead to the total condensation of the vapour phase, and there will remain the univariant system ice—hydrate—solution. The temperature of equilibrium of this system will alter with the pressure, but, as in the case of the melting-point of a simple substance, great differences of pressure will cause only comparatively small changes in the temperature of equilibrium. The change of the eutectic point with the pressure is represented by the line BE; the actual values have not been determined, but the curve must slope towards the pressure axis because fusion is accompanied by diminution of volume, as in the case of pure ice.

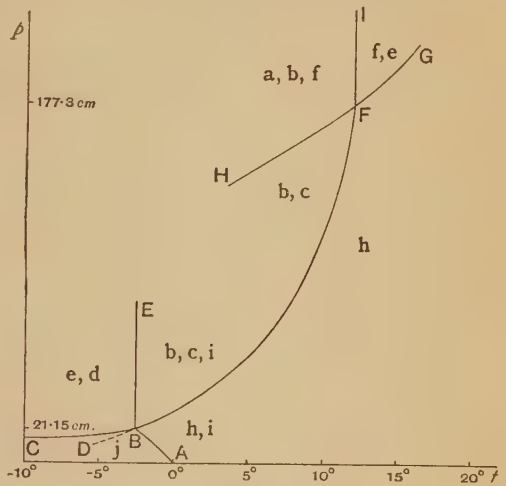


FIG. 86.

A fourth univariant system can be formed at B. This is the system hydrate—solution II.—vapour. The conditions for the existence of

[1] Roozeboom, *Rec. trav. chim. Pays-Bas*, 1884, **3**, 29; 1885, **4**, 65; *Z. physikal. Chem.*, 1888, **2**, 450.

this system are represented by the curve BF, which may therefore be regarded as the vapour-pressure curve of the saturated solution of sulphur dioxide heptahydrate in water. Unlike the curve for iodine trichloride—solution—vapour, this curve cannot be followed to the melting-point of the hydrate. Before this point is reached, a second liquid phase appears, and an invariant system consisting of hydrate—solution I.—solution II.—vapour is formed. We have here, therefore, the phenomenon of melting under the solution as in the case of succinic nitrile and water (p. 128). This point is represented in the diagram by F; the temperature at this point is 12·1°, and the pressure 177·3 cm. The range of stable existence of the hydrate is therefore from — 2·6° to 12·1°; nevertheless, the curve FB has been followed down to a temperature of — 6°, at which point ice formed spontaneously.

So long as the four phases hydrate, two liquid phases, and vapour are present, the condition of the system is perfectly defined. By altering the conditions, however, one of the phases can be made to disappear and a univariant system will then be obtained. Thus, if the vapour phase is made to disappear, the univariant system solution I.—solution II.—hydrate will be left, and the temperature at which this system is in equilibrium will vary with the pressure. This is represented by the curve FI; under a pressure of 225 atm. the temperature of equilibrium is 17·1°. Increase of pressure, therefore, raises the temperature at which the three phases can co-exist.

Again, addition of heat to the invariant system at F will cause the disappearance of the solid phase, and there will be formed the univariant system solution I.—solution II.—vapour. In the case of this system the vapour pressure increases as the temperature rises, as represented by the curve FG. Such a system is analogous to the case of ether and water, or other two partially miscible liquids (p. 90). As the temperature changes, the composition of the two liquid phases will undergo change; but this system has not been studied fully.

The fourth curve, which ends at the quadruple point F, is that representing the vapour pressure of the system hydrate—solution I.—vapour (FH). This curve has been followed to a temperature of 0°, the pressure at this point being 113 cm. The metastable prolongation of GF has also been determined. Although, theoretically, this curve must lie below FH, it was found that the difference in the pressure for the two curves was within the error of experiment.

Bivariant Systems.—The different bivariant systems, consisting of two phases, which can exist within the range of temperature and pressure included in Fig. 86, were given on page 200. The conditions under which these systems can exist are represented by the areas in the diagram, and the fields of the different bivariant systems are indicated by letters, corresponding to the letters on page 200. Just as in the case of one-component systems (p. 29) we found that the field lying between any two curves gave the conditions of existence of that phase which was common to the two curves, so also in the case of two-component systems, a bivariant two-phase system occurs in the field

enclosed [1] by the two curves to which the two phases are common. As can be seen, the same bivariant system can occur in more than one field.

As is evident from Fig. 86, three different bivariant systems are capable of existing in the area HFI; which of these will be obtained will depend on the relative masses of the different phases in the univariant or invariant system. Thus, starting with a system represented by a point on the curve HF, diminution of volume at constant temperature will cause the condensation of a portion of the vapour, which is rich in sulphur dioxide; since this would increase the concentration of sulphur dioxide in the solution, it must be counteracted by the passage of a portion of the hydrate (which is relatively poor in sulphur dioxide) into the solution. If, therefore, the amount of hydrate present is relatively very small, the final result of the compression will be the production of the system *f*, solution I.—vapour. On the other hand, if the vapour is present in relatively small amount, it will be the first phase to disappear, and the bivariant system *a*, hydrate—solution I., will be obtained. Finally, if we start with the invariant system at F, compression will cause the condensation of vapour, while the composition of the two solutions will remain unchanged. When all the vapour has disappeared, the univariant system hydrate—solution I.—solution II. will be left. If, now, the pressure is still further increased, while the temperature is kept below 12°, more and more hydrate must be formed at the expense of the two liquid phases (because 12° is the lower limit for the coexistence of the two liquid phases), and if the amount of the solution I. (containing excess of sulphur dioxide) is relatively small, it will disappear before solution II., and there will be obtained the bivariant system hydrate—solution II. (bivariant system *b*).

In a similar manner, account can be taken of the formation of the other bivariant systems.

A behaviour similar to that of sulphur dioxide and water is shown by chlorine and water and by bromine and water, although these have not been so fully studied.[2] In the case of hydrogen bromide and water, and of hydrogen chloride and water, a hydrate, viz. $HBr,2H_2O$ and $HCl,2H_2O$, is formed which possesses a congruent melting-point, as in the case of iodine trichloride. In these cases, therefore, a retroflex curve is obtained. Further, just as in the case of the chlorides of iodine the upper branch of the retroflex curve ended in a eutectic point, so also in the case of the hydrate $HBr,2H_2O$ the upper branch of the curve ends in a eutectic point at which the system dihydrate—monohydrate—solution—vapour can exist. Before the melting-point of the monohydrate is reached, two liquid phases are formed, as in the case of sulphur dioxide and water.

[1] Two curves "enclose" a field when they form with one another an angle less than two right angles.

[2] Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 450. Compare also the systems sulphur dioxide—halogen, studied by Polak-van der Goot, *Z. physikal. Chem.*, 1913, **84**, 419, and hydrogen sulphide—water, studied by Scheffer, *ibid.*, p. 734.

CHAPTER XII.

SYSTEMS OF THREE COMPONENTS.

General.—It has already been made evident that an increase in the number of the components from one to two gives rise to a considerable increase in the possible number of systems, and introduces not a few complications into the equilibrium relations of these. No less is this the case when the number of components increases from two to three; and although examples of all the possible types of systems of three components have not been investigated, nor, indeed, any one type fully, nevertheless, among the systems which have been studied experimentally, cases occur which not only possess a high scientific interest, but are also of great industrial importance. On account not only of the number, but more especially of the complexity of the systems constituted of three components, no attempt will be made to give a full account, or, indeed, even a survey of all the cases which have been subjected to a more or less complete experimental investigation; on the contrary, only a few of the more important classes will be selected, and the most important points in connection with the behaviour of these described.

On applying the Phase Rule

$$F = n + 2 - r$$

to the systems of three components, we see that in order that the system shall be invariant, no fewer than five phases must be present together, and an invariant system will therefore exist at a *quintuple* point. Since the number of liquid phases can never exceed the number of the components, and since there can be only one vapour phase, it is evident that at the quintuple point, as in the case of other invariant systems, there must always be at least one solid phase present. As the number of phases diminishes, the variability of the system can increase from one to four, so that in the last case the condition of the system will not be completely defined until not only the temperature and the total pressure of the system, but also the concentrations of two of the components have been fixed. Or, instead of the concentrations, the partial pressures of the components may also be taken as independent variables.

Graphic Representation.—Hitherto the concentrations of the components have been represented by means of rectangular co-ordinates, although the numerical relationships have been expressed in two

different ways. In the one case, the concentration of the one component was expressed in terms of a fixed amount of the other component. Thus, the solubility of a salt was expressed by the number of grams of salt dissolved by 100 grams of water or other solvent; and the numbers so obtained were measured along one of the co-ordinates. The second co-ordinate was then employed to indicate the change of another independent variable, *e.g.* temperature. In the other case, the combined weights of the two components A and B were put equal to unity, and the concentration of the one expressed as a fraction of the whole amount. This method allows of the representation of the complete series of concentrations, from pure A to pure B, and was employed, for example, in the graphic representation of the freezing-point curves.

Even in the case of three components, rectangular co-ordinates can also be employed, and, indeed, are the most convenient in those cases where the behaviour of two of the components to one another is very different from their behaviour to the third component; as, for example, in the case of two salts and water. In these cases, the composition of the system can be represented by measuring, along two co-ordinates at right angles to each other, the amounts of each of the two components in a given weight of the third; and the change of the system with the temperature can then be represented by a third axis at right angles to the first two. In those cases, however, where the three components behave in much the same manner towards one another, the rectangular co-ordinates are not at all suitable, and instead of these a *triangular diagram* is employed. Various methods have been proposed for the graphic representation of systems of three components by means of a triangle, but only two of these have been employed to any considerable extent; and a short description of these two methods will therefore suffice.[1]

In the method proposed by Gibbs an equilateral triangle of unit height is used (Fig. 87).[2] The quantities of the different components are expressed as fractional parts of the whole, and the sum of their concentrations is therefore equal to unity, and can be represented by the height of the triangle. The corners of the triangle represent the pure substances, A, B, and C respectively. A point on one of the sides of the triangle will give the composition of a mixture in which only two components are present, while a point within the triangle will represent the composition of a ternary mixture. Since every point within the triangle has the property that the sum of the perpendiculars from that point on the sides of the triangle is equal to unity (the height of the triangle), it is evident that the composition of a ternary mixture can be represented by fixing a point within the triangle such that the lengths of the *perpendiculars* from the point to the sides of the triangle are equal respectively to the fractional amounts of the

[1] G. G. Stokes, *Proc. Roy. Soc.*, 1891, **49**, 174; Gibbs, *Trans. Conn. Acad.*, 1876, **3**, 176; Roozeboom, *Z. physikal. Chem.*, 1894, **15**, 147. For another suggested method of representation, see Lodočnikov, *Z. anorgan. Chem.*, 1926, **151**, 185.

[2] This figure has been taken from Ostwald's *Lehrbuch*, II., **2**, 984.

three components present; the fractional amount of A, B, or C being represented by the perpendicular distance from the side of the triangle *opposite* the corners A, B, and C respectively.

The location of this point is simplified by dividing the normals from each of the corners on the opposite side into ten or one hundred parts, and drawing through these divisions lines at right angles to the normal and parallel to the sides of the triangle. A network of rhombohedra is thus obtained, and the position of any point can be read off in practically the same manner as in the case of rectangular co-ordinates. Thus the point P in Fig. 87 represents a ternary mixture of the composition A = 0·5, B = 0·3, C = 0·2; the perpendiculars P*a*,

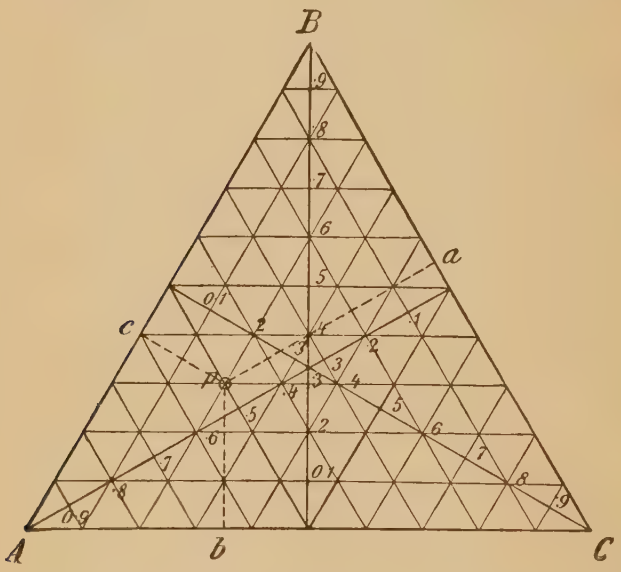


Fig. 87.

P*b*, and P*c* being equal respectively to 0·5, 0·3, and 0·2 of the height of the triangle.

Another method of representation, due to Roozeboom, consists in employing an equilateral triangle, the length of whose *side* is made equal to unity, or one hundred; the sum of the fractional or percentage amounts of the three components being represented therefore by a side of the triangle. In this case the composition of a ternary mixture is obtained by determining, not the *perpendicular* distance of a point P from the three sides of the triangle, but the distance in a direction *parallel* to the sides of the triangle (Fig. 88). Conversely, in order to represent a mixture consisting of *a*, *b*, and *c* parts of the components A, B, and C respectively, one side of the triangle, say AB, is first of all divided into ten or one hundred parts; a portion, B*x* = *a*, is then

measured off, and represents the amount of A present. Similarly, a portion, $Ax' = b$, is measured off and represents the fractional amount of B, while the remainder, $xx' = c$, represents the amount of C. From x and x' lines are drawn parallel to the sides of the triangle, and the point of intersection, P, represents the composition of the ternary mixture of given composition; for, as is evident from the figure, the distance of the point P from the three sides of the triangle, when measured in directions *parallel* to the sides, is equal to a, b, and c respectively. From the division marks on the side AB it is seen that the point P in this figure represents a mixture of 0·5 parts of A, 0·2 parts of B, and 0·3 parts of C. The employment of a right-angled isosceles triangle has also been suggested,[1] but is not in general use.

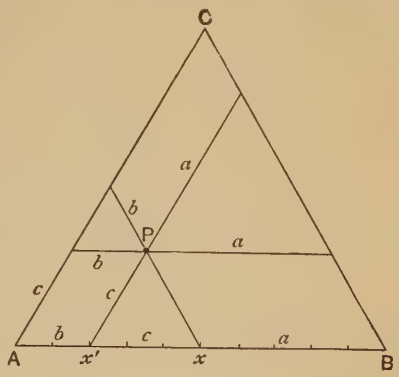


FIG. 88.

In employing the triangular diagram, it will be of use to note a property of the equilateral triangle. A line drawn from one corner of the triangle to the opposite side represents the composition of all mixtures in which the *relative* amounts of two of the components remain unchanged. Thus, as Fig. 89 shows, if the component C is

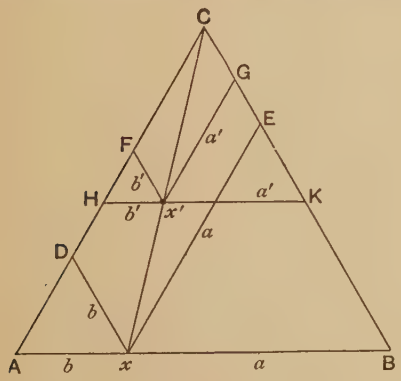


FIG. 89.

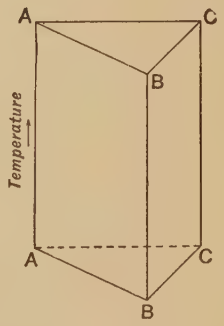


FIG. 90.

added to a mixture x, in which A and B are present in the proportions of $a : b$, a mixture x', which is thereby obtained, also contains A and B in the ratio $a : b$. For the two triangles ACx and BCx are similar to

[1] Roozeboom, *Z. physikal. Chem.*, 1893, **12**, 369.

the two triangles HCx' and KCx' ; and, therefore, Ax : Bx = Hx' : Kx'. But Ax = Dx and Bx = Ex ; further, Hx' = Fx' and Kx' = Gx'. Therefore, Dx : Ex = Fx' : Gx' = b : a. At all points on the line Cx, therefore, the ratio of A to B is the same.

If it is desired to represent at the same time the change of another independent variable, *e.g.* temperature, this can be done by measuring the latter along axes drawn perpendicular to the corners of the triangle. In this way a right prism (Fig. 90) is obtained, and each section of this cut parallel to the base represents therefore an *isothermal surface*.

CHAPTER XIII.

SOLUTIONS OF LIQUIDS IN LIQUIDS.

We have already seen (p. 89) that when two liquids are brought together, they may mix in all proportions and form one homogeneous liquid phase; or, only partial miscibility may occur, and two phases be formed consisting of two mutually saturated solutions. In the latter case, the concentration of the components in either phase and also the vapour pressure of the system had, at a given temperature, perfectly definite values. In the case of three liquid components, a similar behaviour may be found, although complete miscibility of three components with the formation of only one liquid phase is of much rarer occurrence than in the case of two components. When only partial miscibility occurs, various cases are met with according as the three components form one, two, or three pairs of partially miscible liquids. Further, when two of the components are only partially miscible, the addition of the third may cause either an increase or a diminution in the mutual solubility of these. An increase in the mutual solubility is generally found when the third component dissolves readily in each of the other two; but when the third component dissolves only sparingly in the other two, its addition diminishes the mutual solubility of the latter (see p. 97).

We shall consider here only a few examples illustrating the three chief cases which can occur, viz. (1) A and B, and also B and C are miscible in all proportions, while A and C are only partially miscible; (2) A and B are miscible in all proportions, but A and C and B and C are only partially miscible; (3) A and B, B and C, and A and C are only partially miscible. A, B, and C here represent the three components.

1. *The three components form only one pair of partially miscible liquids.*

An example of this is found in the three substances: chloroform, water, and acetic acid.[1] Chloroform and acetic acid, and water and acetic acid, are miscible with each other in all proportions, but chloroform and water are only partially miscible with each other. If, therefore, chloroform is shaken with a larger quantity of water than it can dissolve, two layers will be formed consisting one of a saturated solution of water in chloroform, the other of a saturated solution of chloroform in water. The composition of these two solutions at a

[1] C. R. A. Wright, *Proc. Roy. Soc.*, 1891, **49**, 174; 1892, **50**, 375.

temperature of about 18° will be represented by the points *a* and *b* in Fig. 91 ; *a* representing a solution of the composition : chloroform, 99 per cent., water, 1 per cent. ; and *b* a solution of the composition : chloroform, 0·8 per cent., water, 99·2 per cent. When acetic acid is added, it distributes itself between the two liquid layers, and two conjugate *ternary* solutions, consisting of chloroform, water, and acetic acid are thereby produced which are in equilibrium with each other, and the composition of which will be represented by two points inside the triangle. In this way a series of pairs of ternary solutions will be obtained by the addition of acetic acid to the mixture of chloroform and water. By this addition, also, not only do the two liquid phases become increasingly rich in acetic acid, but the mutual solubility of the chloroform and water increases ; so that the layer *a* becomes relatively richer in water, and layer *b* relatively richer in chloroform. This is seen from the following table, which gives the percentage composition of different conjugate ternary solutions at 18° :—

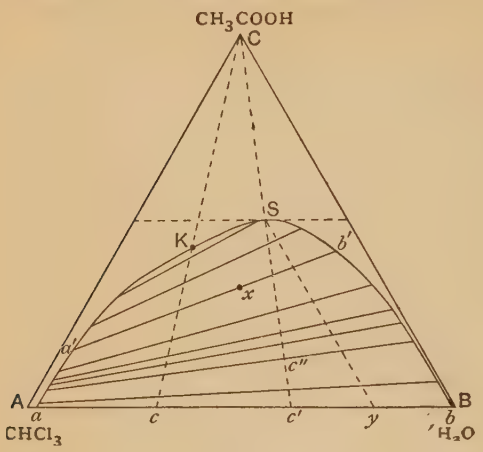


FIG. 91.

Heavier layer.			Lighter layer.		
Chloroform.	Water.	Acetic acid.	Chloroform.	Water.	Acetic acid.
99·01	0·99	0	0·84	99·16	0
91·85	1·38	6·77	1·21	73·69	25·10
80·00	2·28	17·72	7·30	48·58	44·12
70·13	4·12	25·75	15·11	34·71	50·18
67·15	5·20	27·65	18·33	31·11	50·56
59·99	7·93	32·08	25·20	25·39	49·41
55·81	9·58	34·61	28·85	23·28	47·87

By the continued addition of acetic acid, the composition of the successive conjugate solutions in equilibrium with each other becomes, as the table shows, more nearly the same, and a point is at length reached at which the two solutions become identical. This will therefore be a *critical point* (p. 91). Increased addition of acetic acid beyond this point will lead to a single homogeneous solution.

These relationships are represented graphically by the so-called binodal[1] curve *a*K*b* (Fig. 91). The points on the branch *a*K represent the composition of the solutions relatively rich in chloroform (heavier layer), those on the curve *b*K the composition of solutions relatively rich in water (lighter layer); and the points on these two branches representing conjugate solutions are joined together by "tie-lines." Thus, the points *a'b'* represent conjugate solutions, and the line *a'b'* is a tie-line.

Since acetic acid, when added to a heterogeneous mixture of chloroform and water, does not enter in equal amounts into the two layers, but in amounts depending on its coefficient of distribution between chloroform and water,[2] the tie-lines will not be parallel to AB, but will be inclined at an angle. As the solutions become more nearly the same, the tie-lines diminish in length, and at last, when the conjugate solutions become identical, shrink to a point. For the reason that the tie-lines are, in general, not parallel to the side of the triangle, the critical point at which the tie-line vanishes will not be at the summit of the curve, but somewhere below this, as represented by the point K.

The curve *a*K*b*, further, forms the boundary between the heterogeneous and homogeneous systems. A mixture of chloroform, water, and acetic acid, represented by any point outside the curve *a*K*b*, will form only one homogeneous phase; while any mixture represented by a point within the curve will separate into two layers having the composition represented by the ends of the tie-line passing through that point. Thus, a mixture of the total composition *x* will separate into two layers having the composition *a'* and *b'* respectively.

Since three components existing in three phases (two liquid and a vapour phase) constitute a bivariant system, the final result, *i.e.* the composition of the two layers and the total vapour pressure, will not depend merely on the temperature, as in the case of two-component systems (p. 90), but also on the composition of the initial mixture. At constant temperature, however, all mixtures, the composition of which is represented by a point on one and the same tie-line, will separate into the same two liquid phases, although the relative *amounts* of the two phases will vary. If we omit the vapour phase, the condition of the system will depend on the pressure as well as on the temperature and composition of the initial mixture. By keeping the pressure constant, *e.g.* at atmospheric pressure (by working with open vessels), the system again becomes bivariant. We see, therefore, that the position of the curve *a*K*b*, or, in other words, the composition

[1] Because on this curve there are always two related values of the solubility, the curve is called a binodal curve, to distinguish it from an ordinary solubility curve.

[2] The distribution coefficient will not remain constant because, apart from other reasons, the mutual solubility of chloroform and water is altered by the addition of the acid. This increase in the mutual solubility of two liquids by the addition of a third substance is of great importance, both scientifically and industrially; see Timmermans, *Z. physikal. Chem.*, 1907, **58**, 129. See also Chap. VII.

of the different conjugate ternary solutions, will vary with the temperature, and only with the temperature, if we assume either constancy of pressure or the presence of the vapour phase. Since at the critical point the condition is imposed that the two liquid phases become identical, one degree of freedom is thereby lost, and therefore only one degree of freedom remains. The critical point, therefore, depends on the temperature, and only on the temperature; always on the assumption, of course, that the pressure is constant, or that a vapour phase is present. Fig. 91, therefore, represents an isothermal (p. 208).

It is of importance to note that the composition of the different ternary solutions obtained by the addition of acetic acid to a heterogeneous mixture of chloroform and water, will depend not only on the amount of acetic acid added, but also on the relative amounts of chloroform and water at the commencement. Suppose, for example, that we start with chloroform and water in the proportions represented by the point c' (Fig. 91). On mixing these, two liquid layers having the composition a and b respectively will be formed. Since by the addition of acetic acid the relative amounts of these two substances in the system as a whole cannot undergo alteration, the total composition of the different ternary systems which will be obtained must be represented by a point on the line Cc' (p. 207). Thus, for example, by the addition of acetic acid a system may be obtained, the total composition of which is represented by the point c''. Such a system, however, will separate into two conjugate ternary solutions, the composition of which will be represented by the ends of the tie-line passing through the point c''. So long as the total composition of the system lies below the point S, *i.e.* the point of intersection of the line Cc' with the boundary curve, two liquid layers will be formed; while all systems having a total composition represented by a point on the line Cc', above S, will form only one homogeneous solution.

From the figure, also, it is evident that as the amount of acetic acid is increased, the relative amounts of the two liquid layers formed differ more and more until at S a limiting position is reached, when the amount of the one liquid layer dwindles to nought, and only one solution remains.

The same reasoning can be carried through for different initial amounts of chloroform and water, but it would be fruitless to discuss all the different systems which can be obtained. The reason for the preceding discussion was to show that although the addition of acetic acid to a mixture of chloroform and water will, in all cases, lead ultimately to a limiting system, beyond which homogeneity occurs, that point is not necessarily the critical point. On the contrary, in order that addition of acetic acid shall lead to the critical mixture, it is necessary to start with a binary mixture of chloroform and water in the proportions represented by the point c. In this case, addition of acetic acid will give rise to a series of conjugate ternary solutions, the composition of which will gradually approach to one another, and at last become identical.

From the foregoing it will be evident that the amount of acetic acid required to produce a homogeneous solution will depend on the relative amounts of chloroform and water with which we start, and can be ascertained by joining the corner C with the point on the line AB representing the total composition of the initial binary system. The point where this line intersects the boundary curve *a*K*b* will indicate the minimum amount of acetic acid which, under these particular conditions, is necessary to give one homogeneous solution.

Retrograde Solubility.—As a consequence of the fact that acetic acid distributes itself unequally between chloroform and water, and that the critical point K, therefore, does not lie at the summit of the curve, it is possible to start with a homogeneous solution in which the percentage amount of acetic acid is greater than at the critical point, and to pass from this first to a heterogeneous and then again to a homogeneous system merely by altering the relative amounts of chloroform and water. This phenomenon, to which the term *retrograde solubility* is applied, will be observed not only in the case of chloroform, water, and acetic acid, but in all other systems in which the critical point lies below the highest point of the boundary curve for heterogeneous systems. This will be seen from the diagram, Fig. 92. Starting with the homogeneous system represented by *x*, in which, therefore, the concentration of C is greater than in the critical mixture (K), if the relative amounts of A and B are altered in the direction *xx'*, while the amount of C is maintained constant, the system will become heterogeneous when the composition reaches the point *y*, and will remain heterogeneous with changing composition until the point *y'* is passed, when it will again become homogeneous. If the relative concentration of C is increased above that represented by the line SS, this phenomenon will, of course, no longer be observed.

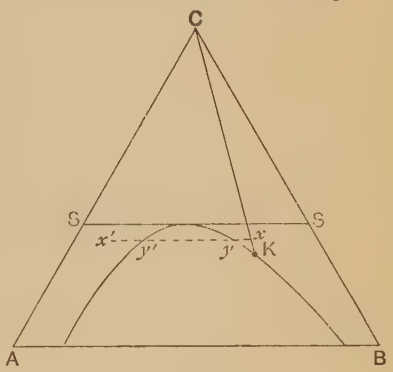


FIG. 92.

Relationships similar to those described for chloroform, water, and acetic acid are also found in the case of a number of other trios, *e.g.* ether, water, and alcohol; chloroform, water, and alcohol.[1] They have also been observed in the case of a considerable number of molten metals.[2] Thus, molten lead and silver, as well as molten zinc and silver, mix in all proportions; but molten lead and zinc are only partially miscible with each other. When melted together, therefore, the

[1] Bancroft, *Physical Review*, 1895, **3**, 21; Schreinemakers, *Z. physikal. Chem.*, 1897, **23**, 652, and subsequent volumes.
[2] C. R. A. Wright, *Proc. Roy. Soc.*, 1889-93.

last two metals will separate into two liquid layers, one rich in lead, the other rich in zinc. If silver is now added, and the temperature maintained above the freezing-point of the mixture, the silver passes for the most part, in accordance with the law of distribution, into the upper layer, which is rich in zinc; silver being more soluble in molten zinc than in molten lead. This is clearly shown by the following figures:—[1]

Heavier alloy.			Lighter alloy.		
Percentage amount of			Percentage amount of		
Silver.	Lead.	Zinc.	Silver.	Lead.	Zinc.
1·25	96·69	2·06	38·91	3·12	57·97
1·71	96·43	1·86	45·01	3·37	51·62
5·55	93·16	1·29	54·93	4·21	40·86

The numbers in the same horizontal row give the composition of the conjugate alloys, and it is evident that the upper layer consists almost entirely of silver and zinc. On allowing the mixture to cool slightly, the upper layer solidifies first, and can be separated from the still molten lead layer. It is on this behaviour of silver towards a mixture of molten lead and zinc that the Parkes's method for the desilverisation of lead depends.[2] If aluminium is also added, a still larger proportion of silver passes into the lighter layer, and the desilverisation of the lead is more complete.[3]

The Influence of Temperature.—As has already been said, a ternary system existing in three phases possesses two degrees of freedom; and the state of the system is therefore dependent not only on the relative concentration of the components, but also on the temperature. As the temperature changes, therefore, the boundary curve of the heterogeneous system will also alter; and in order to represent this alteration, use may be made of the right prism, in which the temperature is measured upwards. In this way the boundary curve (binodal curve), passes into a boundary surface (or binodal surface), as shown in Fig. 93. In this figure the curve *akb* is the isothermal for the ternary system; the curve *a*K*b* shows the change in the *binary* system AB with the temperature, with a critical point at K. This curve has the same meaning as those given in Chapter VII. The curve *k*K is a critical curve joining together the critical points of the different isothermals. In such a case as is shown in Fig. 93, there does not exist any real critical temperature for the ternary system, for as the temperature is raised, the amount of C in the "critical" solution becomes less and less, and at K only two components, A and B, are present. In the

[1] C. R. A. Wright, *Proc. Roy. Soc.*, 1892, **50**, 390.
[2] Bodländer, *Berg- und Hüttenmänn. Ztg.*, 1897, **56**, 331.
[3] C. R. A. Wright, *Proc. Roy. Soc.*, 1892, **50**, 390.

case, however, represented in Fig. 94, a real ternary critical point is found. In this figure *ak'b* is an isothermal, *ak''b* is the curve for the binary system, and K is the ternary critical point. All points outside the helmet-shaped boundary surface represent homogeneous ternary solutions, while all points within the surface belong to heterogeneous systems. Above the temperature of the point K, the three compon-

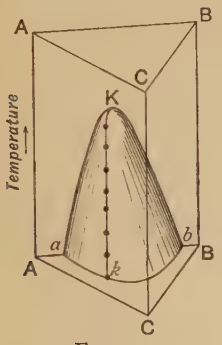


FIG. 93.

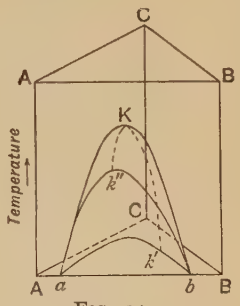


FIG. 94.

ents are miscible in all proportions. An example of a ternary system yielding such a boundary surface is that consisting of phenol, water, and acetone.[1] In this case the critical temperature K is 92°, and the composition at this ternary critical point is—

Water, 59 per cent.
Acetone, 12 ,,
Phenol, 29 ,,

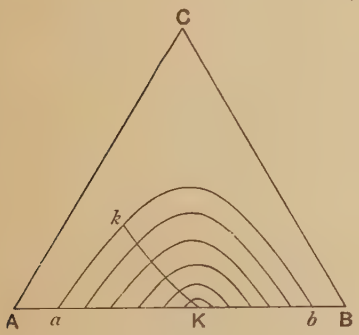


FIG. 95.

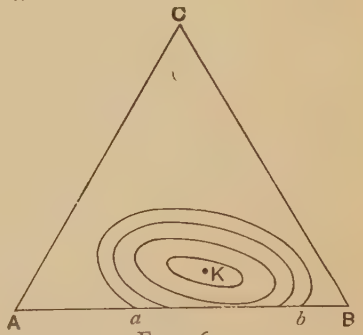


FIG. 96.

The difference between the two classes of systems just mentioned is seen very clearly by a glance at the Figs. 95 and 96, which show the projection of the isothermals on the base of the prism. In Fig. 95, the projections yield paraboloid curves, the two branches of which are cut

[1] Schreinemakers, *Z. physikal. Chem.*, 1900, **33**, 78.

by one side of the triangle; and the critical point is represented by a point on this side. In the second case (Fig. 96), however, the projections of the isothermals form ellipsoidal curves surrounding the supreme critical point, which now lies *inside the triangle*. At lower temperatures these isothermal boundary curves are cut by a side of the triangle; at the critical temperature, k'', of the binary system AB, the boundary curve *touches* the side AB, while at still higher temperatures the boundary curve comes to lie entirely within the triangle. At any given temperature, therefore, between the critical point of the binary system (k''), and the supreme critical point of the ternary system (K), each pair of the three components is miscible in all proportions; for the region of heterogeneous systems is now bounded by a closed curve lying entirely within the triangle. Outside this curve only homogeneous systems are found. Binary mixtures, therefore, represented by any point on one of the sides of the triangle must be homogeneous, for they all lie outside the boundary curve for heterogeneous states.

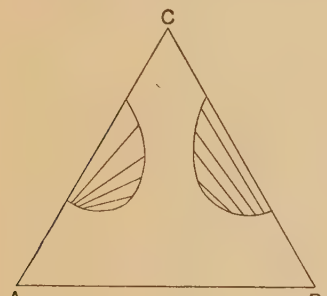


FIG. 97.

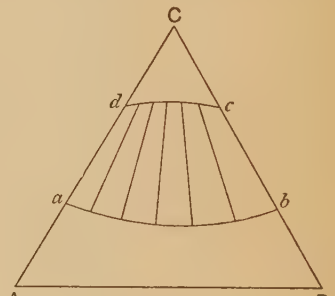


FIG. 98.

2. *The three components can form two pairs of partially miscible liquids.*

In the case of the three components water, alcohol, and succinic nitrile, water and alcohol are miscible in all proportions, but not so water and succinic nitrile, or alcohol and succinic nitrile.

As we have already seen (p. 127), water and succinic nitrile can form two liquid layers between the temperatures 18·5° and 55·5°; while alcohol and nitrile can form two liquid layers between 13° and 31°. If, then, between these two temperature limits, alcohol is added to a heterogeneous mixture of water and nitrile, or water is added to a mixture of alcohol and nitrile, two heterogeneous ternary systems will be formed, and two binodal curves will be obtained in the triangular diagram, as shown in Fig. 97.[1] On changing the temperature, the binodal curves will also undergo alteration, in a manner similar to that just discussed. As the temperature falls, the two curves will

[1] Schreinemakers, *Z. physikal. Chem.*, 1898, **27**, 95.

spread out more and more into the centre of the triangle, and may at last meet one another; while at still lower temperatures we may imagine the curves still further expanding so that the two heterogeneous regions flow into each other and form a *band* on the triangular diagram (Fig. 98). This, certainly, has not been realised in the case of the three components mentioned, because at a temperature higher than that at which the two heterogeneous regions could fuse together, solid separates out.

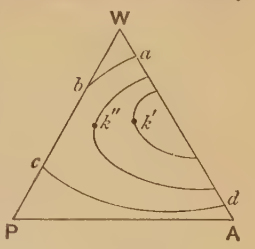


FIG. 99.

The gradual expansion of a paraboloid into a band-like area of heterogeneous ternary systems has, however, been observed in the case of water, phenol, and aniline.[1] In Fig. 99 are shown three isothermals, viz. those for 148°, 95°, and 50°. At 148° water and aniline form two layers having the composition

Water, 83·5 per cent. / Aniline, 16·5 ,, } and { water, 20 per cent. / aniline, 80 ,,

and the critical point k' has the composition

Water, 65; phenol, 13·2; aniline, 21·8 per cent.

At 95° the composition of the two binary solutions is

Water, 93 per cent. / Aniline, 7 ,, } and { water, 8 per cent. / aniline, 92 ,,

while the point k'' has the composition

Water, 69·9; phenol, 26·6; aniline, 3·5 per cent.

At 50° the region of heterogeneous states now forms a band, and the two layers formed by water and aniline have the composition

Water, 96·5 per cent. / Aniline, 3·5 ,, } and { water, 5·5 per cent. / aniline, 94·5 ,,

while the two layers formed by water and phenol have the composition

Water, 89 per cent. / Phenol, 11 ,, } and { water, 38 per cent. / phenol, 62 ,,

All mixtures of water, phenol, and aniline, therefore, the composition of which is represented by any point within the band *abcd*, will form two ternary solutions; while if the composition is represented by a point outside the band, only one homogeneous solution will be produced.

3. *The three components form three pairs of partially miscible liquids.* The third chief case which can occur is that no two of the components are completely miscible with each other. In this case, therefore, three paraboloid binodal curves will be obtained, as shown in

[1] Schreinemakers, *Z. physikal. Chem.*, 1899, **29**, 577.

Fig. 100. If we imagine these three curves to expand in towards the centre of the triangle, as might happen, for example, by lowering the temperature, a point will be reached at which the curves partly overlap, and we shall get the appearance shown in Fig. 101.

The points *a*, *b*, and *c* represent the points where the three curves cut, and the triangle *abc* is a region where the curves overlap. From this diagram we can see that any mixture having a composition represented by a point in one of the clear spaces at the corners of the larger triangle, will form a homogeneous solution; if the composition corresponds to any point lying in one of the quadrilateral regions x_1, x_2, or x_3, two ternary solutions will be formed; while, if the composition is represented by any point in the inner triangle, separation into three layers will occur.

Since in the clear regions at the corners of the triangle we have three components in two phases, liquid and vapour, the systems have

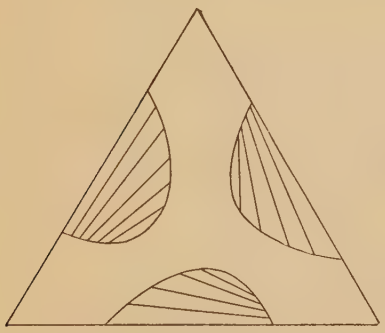


Fig. 100.

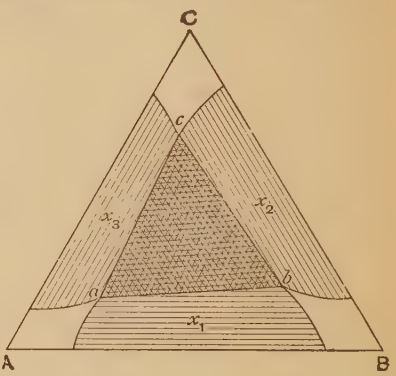


Fig. 101.

three degrees of freedom. At constant temperature, therefore, the condition of the system is not defined until the concentrations of two of the components are fixed. A system belonging to one of the quadrilateral spaces has, as we have seen, two degrees of freedom; besides the temperature, one concentration must be fixed. Lastly, a system the composition of which falls within the inner triangle *abc*, will form three layers, and will therefore possess only one degree of freedom. If the temperature is fixed, the composition of the three layers is also determined, viz. that of the points *a*, *b*, and *c* respectively; and a change in the composition of the original mixture can lead only to a difference in the relative amounts of the three layers, not to a difference in their composition.

An example of a system which can form three liquid phases is found in water, ether, and succinic nitrile.[1]

[1] Schreinemakers, *Z. physikal. Chem.*, 1898, **25**, 543. See also Holmes, *J. Chem. Soc.*, 1918, **113**, 263.

CHAPTER XIV.

PRESENCE OF SOLID PHASES.

A. **The Ternary Eutectic Point.**—In passing to the consideration of those ternary systems in which one or more solid phases can exist together with one liquid phase, we shall first discuss not the solubility curves, but the simpler relationships met with at the freezing-point. That is, we shall first of all examine the freezing-point curves of ternary systems.

Since it is necessary to take into account not only the changing composition of the liquid phase, but also the variation of the temperature, we shall employ the right prism for the graphic representation of the systems, as shown in Fig. 102. A, B, and C in this figure, therefore, denote the melting-points of the pure components. If we start with the component A at its melting-point, and add B, which is capable of dissolving in liquid A, the freezing point of A will be lowered; and, similarly, the freezing-point of B by addition of A. In this way we get the freezing-point curve Ak_1B for the binary system; k_1 being a eutectic point. This curve will, of course, lie in the plane formed by one face of the prism. In a similar manner we obtain the freezing-point curves Ak_2C and Bk_3C. These curves give the composition of the binary liquid phases in equilibrium with one of the pure components, or, at the eutectic points, with a mixture of two solid components. If to the system represented say by the point k_1, a small quantity of the third component, C, is added, the temperature at which the two solid phases A and B can exist in equilibrium with the liquid phase is lowered; and this depression of the eutectic point is all the greater the larger the addition of C. In this way we obtain the curve k_1K, which slopes inwards and downwards, and indicates the varying composition of the ternary liquid phase with which a mixture of solid A and B are in equilibrium. Similarly, the curves k_2K and k_3K are the corresponding eutectic curves for A and C, and B and C in equilibrium with ternary solutions. At the point K, the three solid components

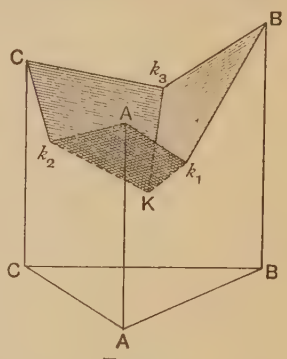


FIG. 102.

are in equilibrium with the liquid phase; and this point, therefore, represents *the lowest temperature attainable with the three components given*. Each of the ternary eutectic curves, as they may be called, is produced by the intersection of two surfaces, while at the ternary eutectic point, three surfaces, viz. Ak_1Kk_2, Bk_1Kk_3, and Ck_1Kk_3 intersect. Any point on one of these surfaces represents a ternary solution in equilibrium with only one component in the solid state; the lines or curves of intersection of these represent equilibria with two solid phases, while at the point K, the ternary eutectic point, there are three solid phases in equilibrium with a liquid and a vapour phase. The surfaces just mentioned represent bivariant systems. One component in the solid state can exist in equilibrium with a ternary liquid phase under varying conditions of temperature and concentration of the components in the solution; and before the state of the system is defined, these two variables, temperature and composition of the liquid

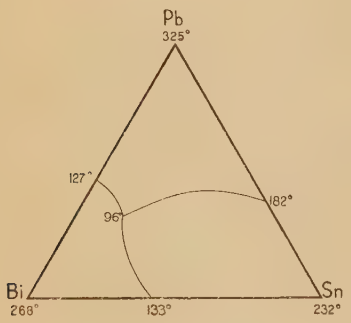


FIG. 103.

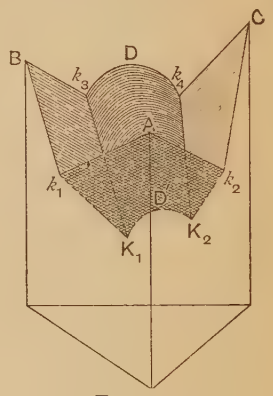


FIG. 104.

phase, must be fixed. On the other hand, the curves formed by the intersection of these planes represent univariant systems; at a given temperature two solid phases can exist in equilibrium with a ternary solution, only when the latter has a definite composition. Lastly, the ternary eutectic point, K, represents an invariant system; three solid phases can exist in equilibrium with a ternary solution, only when the latter has one fixed composition and when the temperature has a definite value. This eutectic point, therefore, has a perfectly definite position, depending only on the nature of the three components.

Instead of employing the prism, the change in the composition of the ternary solutions can also be indicated by means of the *projections* of the curves k_1K, k_2K, and k_3K on the base of the prism, the particular temperature being written beside the different eutectic points and curves. This is shown in Fig. 103.

The numbers which are given in this diagram refer to the eutectic

points for the system bismuth—lead—tin, the data for which are shown in the following table :—[1]

Melting-point of pure metal.	Percentage composition of binary eutectic mixture.			Temperature of binary eutectic point.
	Bi	Pb	Sn	
Bismuth, 268°	55	45	—	Bi—Pb, 127°
Lead, 325°	58	—	42	Bi—Sn, 133°
Tin, 232°	—	37	63	Pb—Sn, 182°

Percentage composition of ternary eutectic mixture.			Temperature of ternary eutectic point.
Bi	Pb	Sn	
52	32	16	96°

Formation of Compounds.—In the case just discussed, the components crystallised out from solution in the pure state. If, however, combination can take place between two of the components, the relationships will be somewhat different; the curves which are obtained in such a case being represented in Fig. 104. From the figure, we see that the two components B and C form a compound, and the freezing-point curve of the binary system has therefore the form shown in Fig. 37 (p. 109). Further, there are two *ternary* eutectic points, K_1 and K_2, the solid phases present being A, B, and compound, and A, C, and compound respectively.

Various examples of this have been studied, and the following table contains some of the data for the system ethylene bromide (A), picric acid (B), and β-naphthol (C), obtained by Bruni.[2]

	Temperature.	Solid phases present.
Point k_1	9·41°	Ethylene bromide, picric acid.
Curve k_1K_1	—	,, ,, ,,
Point K_1	9·32°	Ethylene bromide, picric acid, and β-naphthol picrate.
Curve $K_1D'K_2$	—	Ethylene bromide, β-naphthol picrate.
Point D′	9·75°	,, ,, ,, ,,
Point K_2	8·89°	,, ,, β-naphthol, and picrate.
Curve K_2k_2	—	,, ,, β-naphthol.
Point k_2	9·04°	,, ,, ,,

[1] Charpy, *Compt. rend.*, 1898, **126**, 1569. Compare the curves for the system KNO_3—$NaNO_3$—$LiNO_3$ (H. R. Carveth, *J. Physical Chem.*, 1898, **2**, 209). Also alloys of Pb—Sn—Bi (E. S. Shepherd, *J. Physical Chem.*, 1902, **6**, 527), and of Bi—Sn—Zn (Muzaffar, *J. Chem. Soc.*, 1923, **123**, 2341).

[2] *Gazzetta*, 1898, **28**, II., 520.

From the projection of the curves for ternary solutions on the base of the prism, as shown in Fig. 103, one obtains exact information regarding the *composition* of the different solutions. But the temperature varies from point to point of the curves, and the temperature slope of the curves is not shown in this diagram. The diagram can be improved and made to give fuller information by joining the points of equal temperature, and so producing a series of temperature " contour lines " (see Fig. 111, p. 226).

On the other hand, by sacrificing some of the information regarding the composition of the ternary solutions, it is possible to secure a plane diagram which will give the temperature variations of the system. Thus, by projecting perspectively the curves in Fig. 102 and Fig. 104 not on the base of the prism but on one of the faces, say the face BC, of the prism,[1] a polythermal diagram is obtained which shows the *relative* proportions of the two components B and C in the different systems. The proportion of the component A in the different systems,

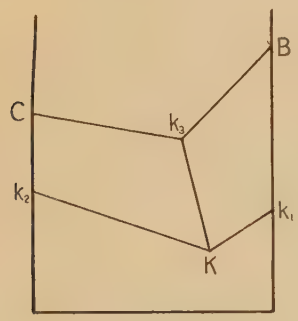


FIG. 105.

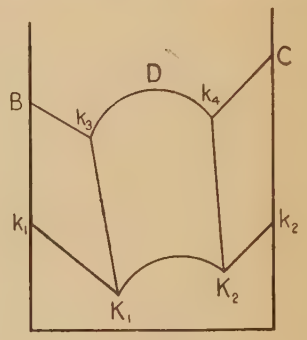


FIG. 106.

however, will not be shown in this diagram ; and the diagram will therefore not convey full information regarding the composition of the solutions. In Figs. 105 and 106 are given the projections of the curves shown in Figs. 102 and 104, on the face of the prism BC. The lettering in these diagrams corresponds with that in Fig. 102 and 104. When no compound is formed between the components B and C, then simple two-branched curves, k_1K and k_2K, are obtained (Fig. 105) ; but when the components B and C give rise to a compound, D, the ternary curve consists of three portions, k_1K_1, K_1K_2, and K_2k_2. The curve Ck_3B in Fig. 105, and Bk_3Dk_4C in Fig. 106, refer, of course, to binary systems.

In the area Ck_2Kk_3 (Fig. 105) the solid phase is component C, while in area Bk_1Kk_3, the solid phase is component B. In Fig. 106, the three areas give the conditions for the stable existence of component B, double salt D, and component C respectively in presence of solution.

[1] This is done by drawing lines parallel to the base of the prism, from the edge AA to the face BC, and passing through the points on the different ternary curves.

It will be clear from the above discussion that if the ternary eutectic curves are projected on a plane parallel with the face BC of the prism, that is, if we express the composition of the solutions in accordance with the formula xA, yB, (100—y) C,[1] then it will be possible to state, from the form of the curve obtained, whether or not the two components present in varying amount crystallise out pure or combine with each other to form a compound. It will be apparent that the projections of the ternary eutectic curves in the manner indicated, will yield a series of curves similar to the binary curves given in Figs. 33, 37, and 43, pp. 103, 109 and 119.

Since, from the method of investigation, the temperatures of the eutectic curves will depend on the melting-point of the third component (A), it is possible, by employing substances with widely different melting-points, to investigate the interaction of the two components (*e.g.* two optical antipodes) B and C over a range of temperature; and thus determine the range of stability of the compound, if one is formed. Since, in some cases, two substances which at one temperature form mixed crystals combine at another temperature to form a definite compound, the relationships which have just been described can be employed, and indeed, have been employed, to determine the temperature at which this change occurs.[2] By means of this method, Adriani found that below 103° *i*-camphoroxime exists as a racemic compound, while above that temperature it occurs as a racemic mixed crystal [3] (*cf.* p. 134).

Thermal Studies on Minerals.—In recent years the application of the Phase Rule to the study of minerals and of compounds and materials (*e.g.* Portland Cement), produced by fusion of their components, has received considerable attention,[4] and a short account will therefore be given here of the equilibria which occur in the ternary system $CaO—Al_2O_3—SiO_2$.[5]

The three components, calcium oxide, aluminium oxide, and silica,

[1] That is, the amounts of B and C are referred to a constant amount of A. It should be remembered that in the triangular diagram a *line* parallel to one of the sides indicates, at a given temperature, a constant amount of the component represented by the opposite corner of the triangle; and hence, points in a *plane*, parallel to one face of a right prism, will indicate, for different temperatures, variation in the amounts of two components, but constancy in the amount of the third. See also Jänecke, *Z. anorgan. Chem.*, 1906, **51**, 132.

[2] Bruni, *Gazzetta*, 1898, **28**, II., 508; 1900, **30**, I., 35.

[3] *Z. physikal. Chem.*, 1900, **36**, 168. For a discussion of mixed crystals in ternary systems, see Schreinemakers, *Arch. néerland*, 1905 [2], **11**, 53; Sahmen, *Z. physikal. Chem.*, 1912, **79**, 421.

[4] Shepherd, Rankin, and Wright, *J. Ind. Eng. Chem.*, 1911, **3**, 211; Rankin and Wright, *Amer. J. Sci.*, 1915 [4], **39**, 1; Andersen, *ibid.*, 1915 [4], **39**, 407; Bowen, *ibid.*, 1915 [4], **40**, 161; 1917 [4], **43**, 115; Rankin and Merwin, *J. Amer. Chem. Soc.*, 1916, **38**, 568; *Amer. J. Sci.*, 1918 [4], **45**, 301; Niggli, *Z. anorgan. Chem.*, 1916, **98**, 241; Ferguson and Merwin, *Amer. J. Sci.*, 1919 [4], **48**, 81, 165; Grahmann, *Jahrb. Min.*, 1920, i. 1; Ferguson and Buddington, *Amer. J. Sci.*, 1920 [4], **50** 131. For melting-point relations of soda—lime—silica glasses, see Morey and Bowen, *T. Soc. Glass Tech.*, 1925, **9**, 226.

[5] Rankin and Wright, *Amer. J. Sci.*, 1915 [4], **39**, 1.

the stable form of which at the melting-point is cristobalite, melt at 2570°, 2050°, and 1625° respectively.[1] These components do not give rise to any mixed crystals, but form a number of binary and of ternary compounds.

The freezing-point curves for the binary systems are shown in Figs. 107, 108, and 109. From Fig. 107 it will be seen that silica and alumina form only one compound, sillimanite, Al_2SiO_5, the melting-point of which, C, lies at 1816°. The eutectics, B and D, occur at 1610° and 1810° respectively. The binary system silica—lime is more complex, there being formed at the temperature of the fusion curve (Fig. 108) three compounds $CaSiO_3$ (curve BDC), $Ca_3Si_2O_7$ (curve CE), and Ca_2SiO_4[2] (curve EFG). The melting-point of $CaSiO_3$ (D) lies at 1540°, and that of Ca_2SiO_4 (F) at 2130°. The compound $Ca_3Si_2O_7$ undergoes transition to Ca_2SiO_4 at 1475° (E). The eutectics, B, C, and G lie at 1436°, 1455°, and 2065° respectively. When a mixture of Ca_2SiO_4 and CaO is cooled below 1900°, combination takes place with formation of Ca_3SiO_5. This compound does not exist in equilibrium with a liquid phase. The two components lime and alumina form a still more complex system and give rise to four compounds stable in contact with a liquid phase. These compounds are $Ca_3Al_2O_6$, $Ca_5Al_6O_{14}$, $CaAl_2O_4$, and $Ca_3Al_{10}O_{18}$. The first compound undergoes decomposition at 1535° (B, Fig. 109), a temperature below its melting-point. The compound $Ca_5Al_6O_{14}$ (D) melts at 1455°, the compound $CaAl_2O_4$ (F) at 1600°, and the compound $Ca_3Al_{10}O_{18}$ (H) at 1720°. The eutectics C, E, G, and I, lie at 1395°, 1400°, 1590°, and 1700° respectively.

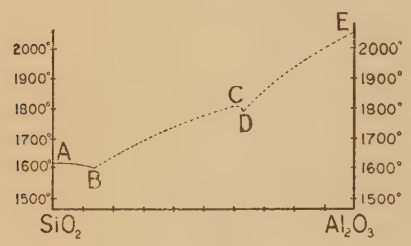


FIG. 107.

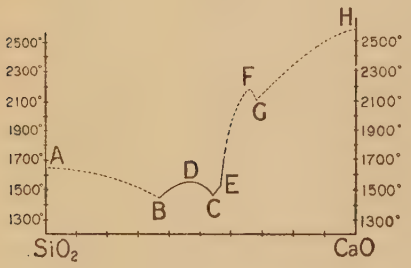


FIG. 108.

For the representation of the ternary equilibria, use may be made of the solid prismatic model, Fig. 110, and of the projection of the ternary curves on the base of the prism, Fig. 111 (*cf.* Fig. 103). The upper corners of the model represent the melting-points of the pure components, and the upper edges of the prism represent the three

[1] See Kanolt, *J. Washington Acad. Sci.*, 1913, 3, 315.

[2] The compound Ca_2SiO_4 occurs in three polymorphic forms, α, β, and γ. The form stable at the melting-point is α.

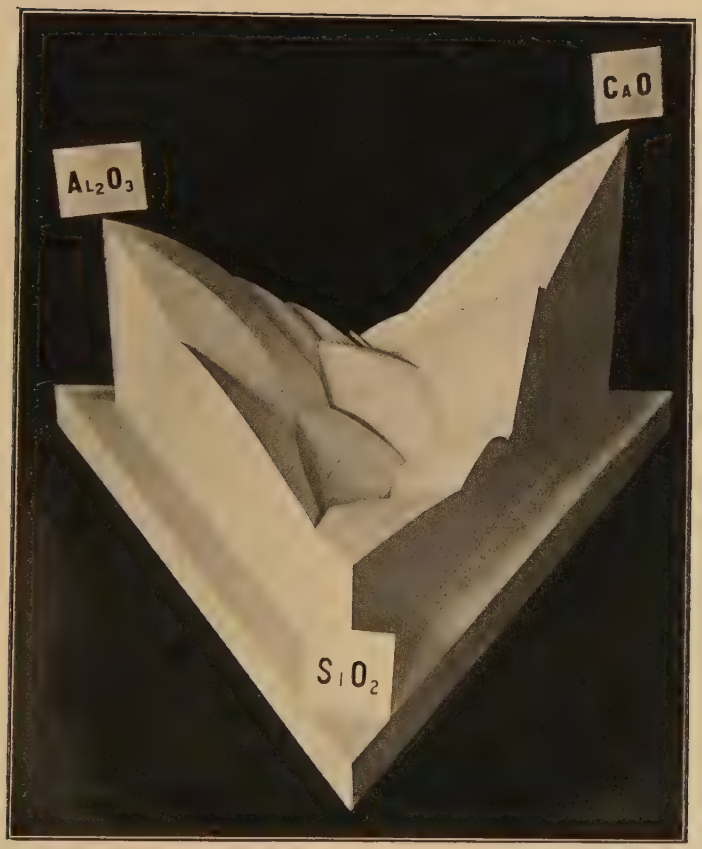


FIG. 110.—Model of systems of CaO—Al_2O_3—SiO_2.

[*To face page* 224.

freezing-point curves for binary systems, corresponding with Figs. 107-109. From each binary eutectic point a line passes inwards and gives the composition of solutions in equilibrium with two solid phases. At the points where three such boundary curves cut, we have a ternary eutectic point. The areas or surfaces on the model or plane diagram give the conditions for the existence of a single solid phase in contact with ternary solutions. Areas which are bounded by a side of the triangle or face of the prism, apply either to a pure component or to a binary compound, while areas situated entirely within the triangle or prism apply to ternary compounds. Two such ternary

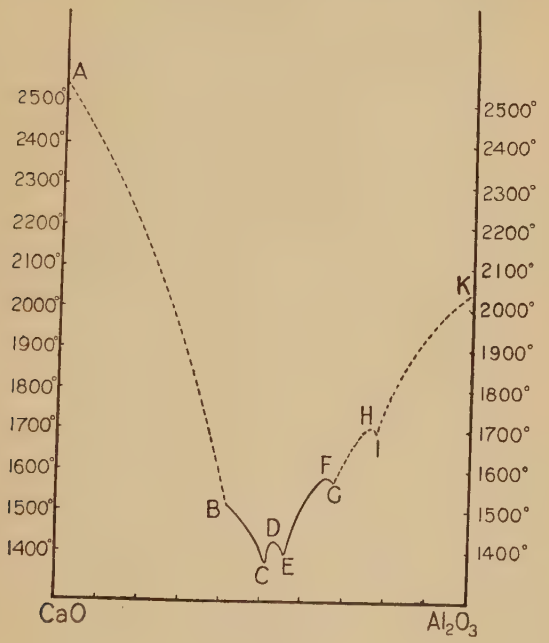


FIG. 109.

compounds have been obtained, both stable at the melting-point, and there are therefore two areas lying entirely within the prism or triangle. The stable ternary compounds are $CaAl_2Si_2O_8$ (anorthite), melting at 1550°, and $Ca_2Al_2SiO_7$, melting at 1590°. A third ternary compound, $Ca_3Al_2SiO_8$, is unstable at the melting-point and is therefore not represented in the diagram or model.

The narrow triangular area lying between the areas for CaO and Ca_2SiO_4 (Fig. 111) refers to the binary compound, Ca_3SiO_5, which makes its appearance at 1900° on the eutectic curve for CaO and Ca_2SiO_4.

The faintly-drawn lines in the triangular diagram (Fig. 111) represent isotherms. By means of these one gains a knowledge of the contour of the surfaces of the solid model.

From a study of the diagram, Fig. 111, and of the model, Fig. 110, it will be possible to predict what will happen when any molten mixture of CaO, Al_2O_3, and SiO_2, is cooled. On cooling a molten mixture the composition of which is represented by a point lying within the triangle, Fig. 111, the mixture will deposit the solid phase (pure component, binary compound, or ternary compound) corresponding to the area in which the point representing the composition of the mixture lies. If the initial composition was not that of the melting-point of a compound,

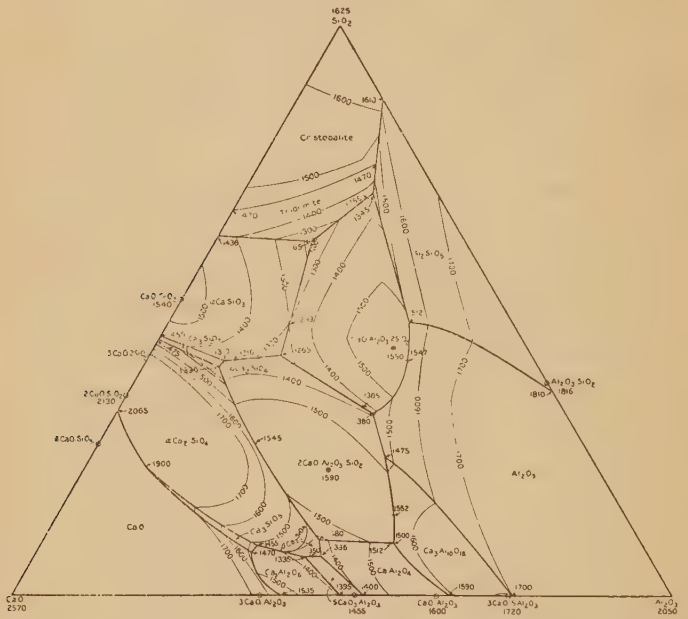


FIG. 111.

the composition of the residual solution will alter as solid is deposited and will follow a path which will ultimately reach one of the eutectic curves. At this point a second solid phase will begin to separate, and the path of crystallisation will follow the eutectic curve to lower temperatures until it reaches a ternary eutectic point, where a third solid phase will be formed and complete solidification will take place at constant temperature and constant composition.

From such an investigation of equilibria as that just described much information is obtained with regard to problems in petrology and mineral formation and the origin of igneous rocks.[1] From the

[1] Bowen, *J. Geol.*, 1915, **23**, Supplement; *ibid.*, 1917, **25**, 209.

data obtained, and their graphic representation (Fig. 111), Rankin and Wright concluded that Portland cement clinker prepared in the ordinary way from lime, silica, and alumina, would be essentially a mixture of Ca_3SiO_5, Ca_2SiO_4, and $Ca_3Al_2O_6$ with some $Ca_5Al_6O_{14}$ and, possibly, a small amount of free CaO. This conclusion was confirmed by the work of the United States Bureau of Standards.

B. **Aqueous Solutions. Formation of Double Salts.**—Owing not only to the theoretical interest but also to the great practical importance attaching to the systems, it is proposed to discuss in the present section systems formed of two salts and water, in which the water is present in relatively large amount and acts as solvent. In studying these systems, one restriction must be made, viz. that the single salts are salts either of the same base or of the same acid; or are, in other words, capable of yielding a common ion in solution. Such a restriction is necessary, because otherwise the system would be one not of three but of four components.

Transition Point.—As is very well known, there exist a number of hydrated salts which, on being heated, undergo apparent partial fusion; and in Chapter XI. the behaviour of such hydrates was more fully studied in the light of the Phase Rule. Glauber's salt, or sodium sulphate decahydrate, for example, on being heated to a temperature of about 32·5°, partially liquefies, owing to the fact that the water of crystallisation is split off and anhydrous sodium sulphate formed, as shown by the equation

$$Na_2SO_4,10H_2O = Na_2SO_4 + 10H_2O.$$

The temperature of 32·5°, it was learned, constitutes a *transition point* for the decahydrate and anhydrous salt plus water; decomposition of the hydrated salt occurring above this temperature, combination of the anhydrous salt and water below it.

Analogous phenomena are met with in systems constituted of two salts and water in which the formation of double salts can take place. Thus, for example, if *d*-sodium potassium tartrate is heated to above 55°, apparent partial fusion occurs, and the two single salts, *d*-sodium tartrate and *d*-potassium tartrate, are deposited, the change which occurs being represented by the equation

$$4NaKC_4O_6H_4,4H_2O = 2Na_2C_4O_6H_4,2H_2O + 2K_2C_4O_6H_4,\tfrac{1}{2}H_2O + 11H_2O.$$

On the other hand, if sodium and potassium tartrates are mixed with water in the proportions shown on the right side of the equation, the system will remain partially liquid so long as the temperature is maintained above 55° (in a closed vessel to prevent loss of water), but on allowing the temperature to fall below this point, complete solidification will ensue, owing to the formation of the hydrated double salt. Below 55°, therefore, the hydrated double salt is the stable

system, while above this temperature the two single salts plus saturated solution are stable.[1]

A similar behaviour is found in the case of the double salt, copper dipotassium chloride ($CuCl_2,2KCl,2H_2O$ or $CuK_2Cl_4,2H_2O$).[2] When this salt is heated to 92°, partial liquefaction occurs, and the original blue plate-shaped crystals give place to brown crystalline needles and white cubes; while on allowing the temperature to fall, re-formation of the blue double salt ensues. The temperature 92° is, therefore, a transition point at which the reversible reaction

$$CuK_2Cl_4,2H_2O \rightleftarrows CuKCl_3 + KCl + 2H_2O$$

takes place.

The decomposition of sodium potassium tartrate, or of copper dipotassium chloride, differs in so far from that of Glauber's salt that *two* new solid phases are formed; and in the case of copper dipotassium chloride, one of the decomposition products is itself a double salt.

In the two examples of double-salt decomposition which have just been mentioned, sufficient water was yielded to cause a partial liquefaction; but other cases are known where this is not so. Thus, when copper calcium acetate is heated to a temperature of 75°, although decomposition of the double salt into the two single salts occurs as represented by the equation [3]

$$CuCa(C_2H_3O_2)_4,8H_2O = Cu(C_2H_3O_2)_2,H_2O + Ca(C_2H_3O_2)_2,H_2O + 6H_2O$$

the amount of water split off is insufficient to give the appearance of partial fusion, and, therefore, only a change in the crystals is observed.

The preceding examples, in which decomposition of the double salt was effected by a rise of temperature, were chosen for first consideration as being more analogous to the case of Glauber's salt; but not a few examples are known where the reverse change takes place, formation of the double salt occurring *above* the transition point, and decomposition into the constituent salts below it. Instances of this behaviour are found in the case of the formation of astracanite from sodium and magnesium sulphates, and of sodium ammonium racemate from the two sodium ammonium tartrates, to which reference will be made later. Between these various systems, however, there is no essential difference; and whether decomposition or formation of the double salt occurs at temperatures above the transition point will of course depend on the heat of change at that point. For, in accordance with van't Hoff's law of movable equilibrium (p. 18), that change will take place at the higher temperature which is accompanied by an absorption of heat. If, therefore, the formation of the double salt from the single salts is accompanied by an absorption of heat, the double salt will be formed from the single salts on raising the

[1] Van Leeuwen, *Z. physikal. Chem.*, 1897, **23**, 35.
[2] Meyerhoffer, *Z. physikal. Chem.*, 1889, **3**, 336; 1890, **5**, 97.
[3] Reicher, *Z. physikal. Chem.*, 1887, **1**, 220.

temperature; but if the reverse is the case, then the double salt on being heated will decompose into the constituent salts.[1]

In those cases where the change at the transition point is accompanied by the taking up or the splitting off of water, *the general rule can be given, that if the water of crystallisation of the two constituent salts together is greater than that of the double salt, the latter will be produced from the former on raising the temperature* (*e.g.* astracanite from sodium and magnesium sulphates); *but if the double salt contains more water of crystallisation than the two single salts, raising the temperature will effect the decomposition of the double salt.* When we seek for the connection between this rule and the law of van't Hoff, it is found in the fact that the heat effect involved in the hydration or dehydration of the salts is much greater than that of the other changes which occur, and determines, therefore, the sign of the total heat effect.

Vapour Pressure. Quintuple Point.—In the case of Glauber's salt, we saw that at a certain temperature the vapour pressure curve of the hydrated salt cuts that of the saturated solution of anhydrous sodium sulphate. That point, it will be remembered, is a quadruple point at which the four phases sodium sulphate decahydrate, anhydrous sodium sulphate, solution, and vapour, can coexist; and is also the point of intersection of the curves for four univariant systems. In the case of the formation of double salts, similar relationships are met with; and also certain differences, due to the fact that we are now dealing with systems of three components. Two cases will be chosen here for brief description, one in which formation, the other in which decomposition of the double salt occurs with rise of temperature.

On heating a mixture of sodium sulphate decahydrate and magnesium sulphate heptahydrate, it is found that at 22° partial liquefaction occurs with formation of astracanite. At this temperature, therefore, there can coexist the five phases

$$Na_2SO_4,10H_2O\ ;\ MgSO_4,7H_2O\ ;\ Na_2Mg(SO_4)_2,4H_2O\ ;$$
$$\text{solution}\ ;\ \text{vapour}.$$

This constitutes, therefore, a *quintuple point;* and since there are three components present in five phases, the system is invariant. This point, also, will be the point of intersection of curves for five univariant systems, which, in this case, must each be composed of four phases. These systems are:—

I. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; vapour.
II. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; solution ; vapour.
III. $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution ; vapour.
IV. $Na_2SO_4,10H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution ; vapour.
V. $Na_2SO_4,10H_2O$; $MgSO_4,7H_2O$; $Na_2Mg(SO_4)_2,4H_2O$; solution.

[1] For other examples of the formation and decomposition of double salts at a transition point, see Roozeboom-Schreinemakers, *Die Heterogenen Gleichgewichte*, III., Part 1.

On representing the vapour pressures of these different systems graphically, a diagram is obtained such as is shown in Fig. 112,[1] the curves being numbered in accordance with the above list. When the system I. is heated, the vapour pressure increases until at the quintuple point the liquid phase (solution) is formed, and it will then depend on the relative amounts of the different phases whether, on further heating, there is formed system III., IV., or V. If either of the first two is produced, we shall obtain the vapour pressure of the solutions saturated with respect to both double salt and one of the single salts; while if the vapour phase disappears, there will be obtained the pressure of the condensed systems formed of double salt, two single salts and solution. This curve, therefore, indicates the *change of the transition point with pressure;* and since, in the ordinary determinations of the transition point in open vessels, we are in reality dealing with condensed systems under the pressure of 1 atm., it will be evident that the transition point does not accurately coincide with the quintuple point (at which the system is under the pressure

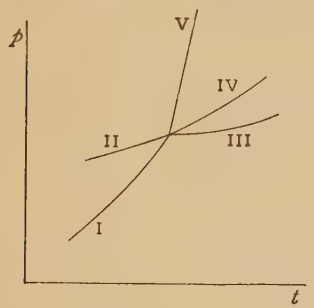


Fig. 112.

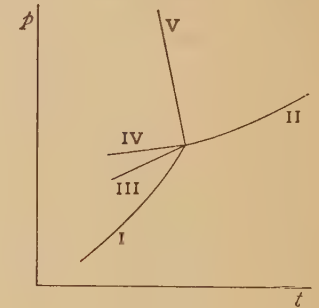


Fig. 113.

of its own vapour). As in the case of other condensed systems, however, pressure has only a relatively slight influence on the temperature of the transition point. Whether or not pressure raises or lowers the transition point will depend on whether transformation is accompanied by an increase or diminution of volume (theorem of Le Chatelier, p. 18). In the case of the formation of astracanite, expansion occurs, and the transition point will therefore be raised by increase of pressure. Although measurements have not been made in the case of this system, the existence of such a curve has been experimentally verified in the case of copper and calcium acetates and water (v. *infra*).[2]

[1] Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 514.

[2] The influence of pressure on the transition point in the case of tachydrite has been determined by van't Hoff, Kenrick, and Dawson (*Z. physikal. Chem.*, 1901, **39**, 27, 34; van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, I., p. 66—Vieweg, 1905). This salt is formed from magnesium chloride and calcium chloride at 22°, in accordance with the equation

$$2MgCl_2 . 6H_2O + CaCl_2 . 6H_2O = Mg_2CaCl_6 . 12H_2O + 6H_2O.$$

Increase of pressure raises the transition point, because the formation of tachydrite is accompanied by increase of volume, the elevation being 0·016° for an increase

The vapour pressure diagram in the case of copper calcium acetate and water (Fig. 113), is almost the reverse of that already discussed. In this case, the double salt decomposes on heating, and the decomposition is accompanied by a contraction. Curve I. is the vapour pressure curve for double salt, two single salts (p. 228), and vapour; curves II. and III. give the vapour pressures of solutions saturated with respect to double salt and one of the single salts; curve IV. is the curve of pressures for the solutions saturated with respect to the two single salts; while curve V. again represents the change of the transition point with pressure. On examining this diagram, it is seen that whereas astracanite could exist both above and below the quintuple point, copper calcium acetate can exist only *below* the quintuple point. This behaviour is found only in those cases in which the double salt is decomposed by rise of temperature, and where the decomposition is accompanied by a diminution of volume.[1]

As already mentioned, the decomposition of copper calcium acetate into the single salts and saturated solution is accompanied by a contraction, and it was therefore to be expected that increase of pressure would *lower* the transition point. This expectation of theory was confirmed by experiment, for van't Hoff and Spring found that although the transition point under atmospheric pressure is about 75°, decomposition of the double salt took place even at the ordinary temperature when the pressure was increased to 6000 atm.[2]

Solubility Curves at the Transition Point.—At the transition point, as has already been shown, the double salt and the two constituent salts can exist in equilibrium with the same solution. The transition point, therefore, must be the point of intersection of two solubility curves; the solubility curve of the double salt and the solubility curve of the mixtures of the two constituent salts. It should be noted here that we are not dealing with the solubility curves of the single salts separately, for since the systems are composed of three components, a single solid phase can, at a given temperature, be in equilibrium with solutions of different composition, and two solid phases in contact with solution (and vapour) are therefore necessary to give a univariant system. The same applies, of course, to the solubility of the double salt; for a double salt also constitutes a single phase, and can therefore exist in equilibrium with solutions of varying composition. If, however, we make the restriction (which we do for the present) that the double salt is not decomposed by water, then the

of pressure of 1 atm. The number calculated from the Clausius-Clapeyron equation (p. 19) is 0·013° for 1 atm.

If one calculates the influence of the pressure of sea-water on the temperature of formation of tachydrite (which is of interest on account of the natural occurrence of this salt), it is found that a depth of water of 1500 metres, exerting a pressure of 180 atm., would alter the temperature of formation of tachydrite by only 3°. The effect is, therefore, comparatively unimportant.

[1] Roozeboom, *Z. physikal. Chem.*, 1887, **1**, 227.

[2] *Z. physikal. Chem.*, 1887, **1**, 227.

solution will contain the constituent salts in the same relative proportions as they are contained in the double salt, and the system may therefore be regarded as one of *two* components, viz. double salt and water. In this case one solid phase is sufficient, with solution and vapour, to give a univariant system; and at a given temperature, therefore, the solubility will have a perfectly definite value.

Since in almost all cases the solubility is determined in open vessels, we shall in the following discussion consider that the vapour phase is absent, and that the system is under a constant pressure, that of the atmosphere. With this restriction, therefore, four phases will constitute an invariant system, three phases a univariant, and two phases a bivariant system.

It has already been learned that in the case of sodium sulphate and water, the solubility curve of the salt undergoes a sudden change in direction at the transition point, and that this is accompanied by a change in the solid phase in equilibrium with the solution. The same behaviour is also found in the case of double salts. To illustrate this, we shall briefly discuss the solubility relations of a few double salts, beginning with one of the simplest cases, that of the formation of rubidium racemate from rubidium *d*- and *l*-tartrates. The solubilities are represented diagrammatically in Fig. 114, the numerical data being contained in the following table, in which the solubility is expressed as the number of gram-molecules $Rb_2C_4H_4O_6$ in 100 gm.-molecules of water:—[1]

Temperature.	Solubility of tartrate mixture.	Solubility of racemate.
25°	13·03	10·91
35°	—	12·63
40·4°	—	13·48
40·7°	13·46	—
54°	13·83	—

In Fig. 114 the curve AB represents the solubility of the racemate, while A′BC represents the solubility of the mixed tartrates. Below the transition point, therefore, the solubility of the racemate is less than that of the mixed tartrates. The solution, saturated with respect to the latter, will be supersaturated with respect to the racemate; and if a nucleus of this is present, racemate will be deposited, and the mixed tartrates, if present in equimolecular amounts, will ultimately entirely disappear, and only racemate will be left as solid phase. The solution will then have the composition represented by a point on the curve AB. Conversely, above the transition point, the saturated solution of the racemate would be supersaturated with respect to the two tartrates, and transformation into the latter would ensue.

[1] Van't Hoff and Müller, *Ber.*, 1898, **31**, 2206.

If, therefore, a solution of equimolecular proportions of rubidium *d*- and *l*-tartrates is allowed to evaporate at a temperature above 40°, a mixture of the two tartrates will be deposited;[1] while at temperatures below 40° the racemate will separate out.

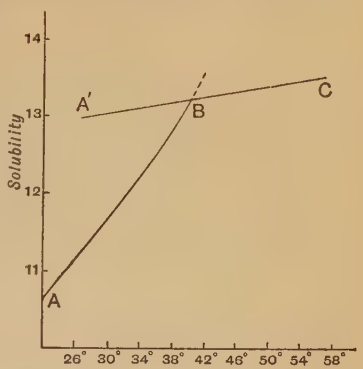


FIG. 114.

Similar relationships are met with in the case of sodium ammonium *d*- and *l*-tartrate and sodium ammonium racemate; but in this case the racemate is the stable form in contact with solution above the transition point (27°).[2] Below the transition point, therefore, the solubility curve of the mixed tartrates will lie below the solubility curve of the racemate. Below the transition point, therefore, sodium ammonium racemate will break up in contact with solution into a mixture of sodium ammonium *d*- and *l*-tartrates. At a higher temperature, 35°, sodium ammonium racemate undergoes decomposition into sodium racemate and ammonium racemate.[3]

The behaviour of sodium ammonium racemate is of interest from the fact that it was the first racemic substance to be resolved into its optically active forms by a process of crystallisation. On neutralising a solution of racemic tartaric acid, half with soda and half with ammonia, and allowing the solution to evaporate, Pasteur[4] obtained a mixture of sodium ammonium *d*- and *l*-tartrates. Since Pasteur was unaware of the existence of a transition point, the success of his experiment was due to the happy chance that he allowed the solution to evaporate at a temperature below 27°; for had he employed a temperature above this, separation of the racemate into the two enantiomorphous forms would not have occurred. For this reason the attempt of Staedel to perform the same resolution met only with failure.[5]

Decomposition of the Double Salt by Water.—In the two cases just described, the solubility relationships at the transition point are of a simpler character than in the case of most double salts. If, at a temperature above the transition point, a mixture of rubidium *d*- and *l*-tartrates in equimolecular proportions is brought in contact with water, a solution will be obtained which is saturated with respect to both enantiomorphous forms; and since the solubility of the two

[1] Traube, *Jahrb. Min. Beil.-Bd.*, **10**, 795.
[2] Van't Hoff and van Deventer, *Z. physikal. Chem.*, 1887, **1**, 165.
[3] For a full discussion of the solubility relations of sodium ammonium racemate, see van't Hoff, *Bildung und Spaltung von Doppelsalzen*, p. 81.
[4] *Annales chim. phys.*, 1848 [3], **24**, 442.
[5] See van't Hoff and van Deventer, *Z. physikal. Chem.*, 1887, **1**, 165.

optical antipodes is identical, and the effect of one on the solubility of the other also the same, the solution will contain equimolecular amounts of the *d*- and *l*-salt. If, now, the solution is cooled down in contact with the solid salts to just below the transition point, it becomes supersaturated with respect to the racemate, and this will be deposited. The solution thereby becomes unsaturated with respect to the mixture of the active salts, and these must therefore pass into solution. As the latter are equally soluble, equal amounts of each will dissolve, and a further quantity of the racemate will be deposited. These processes of solution and deposition will continue until the single tartrates have completely disappeared, and only racemate is left as solid phase. As a consequence of the identical solubility of the two tartrates, therefore, no excess of either form will be left on passing through the transition point. From this it will be evident that the racemate can exist as single solid phase in contact with its saturated solution at the transition point; or, in other words, the racemate is not decomposed by water at the transition point. The same behaviour will evidently be exhibited by sodium ammonium racemate at 27°, for the two enantiomorphous sodium ammonium tartrates have also identical solubility.

Very different, however, is the behaviour of, say, astracanite, or of the majority of double salts; for the solubility of the constituent salts is now no longer the same. If, for example, excess of a mixture of sodium sulphate and magnesium sulphate, in equimolecular proportions, is brought in contact with water below the transition point (22°), more magnesium sulphate than sodium sulphate will dissolve, the solubility of these two salts in a common solution being given by the following figures, which express number of gm.-molecules of the salt in 100 gm.-molecules of water:—[1]

Composition of Solutions Saturated with Respect to $Na_2SO_4,10H_2O$ and $MgSO_4,7H_2O$.

Temperature.	Na_2SO_4.	$MgSO_4$.
18·5°	2·16	4·57
24·5°	3·43	4·68

At the transition point, then, it is evident that the solution contains more magnesium sulphate than sodium sulphate: and this must still be the case when astracanite, which contains sodium sulphate and magnesium sulphate in equimolecular proportions, separates out. If, therefore, the temperature is raised slightly above the transition point, magnesium sulphate and sodium sulphate will pass into solution, the former, however, in larger quantities than the latter, and astracanite

[1] Meyerhoffer, *Z. physikal. Chem.*, 1890, 5, 121.

will be deposited ; and this process will go on until all the magnesium sulphate has disappeared, and a mixture of astracanite and sodium sulphate decahydrate is left as solid phases. Since there are now three phases present, the system is univariant (by reason of the restriction previously made that the pressure is constant and the vapour phase is absent), and at a given temperature the solution will have a definite composition, as given in the following table :—

COMPOSITION OF SOLUTION SATURATED WITH RESPECT TO $Na_2Mg(SO_4)_2,4H_2O$ AND $Na_2SO_4,10H_2O$.

Temperature.	Na_2SO_4.	$MgSO_4$.
22°	2·95	4·70
24·5°	3·45	3·62

From the above figures, therefore, it will be seen that at a temperature just above the transition point a solution in contact with the two solid phases, astracanite and Glauber's salt, contains a relatively smaller amount of sodium sulphate than a pure solution of astracanite would ; for in this case there would be equal molecular amounts of Na_2SO_4 and $MgSO_4$. A solution which is saturated with respect to astracanite alone, will contain more sodium sulphate than the solution saturated with respect to astracanite plus Glauber's salt, and the

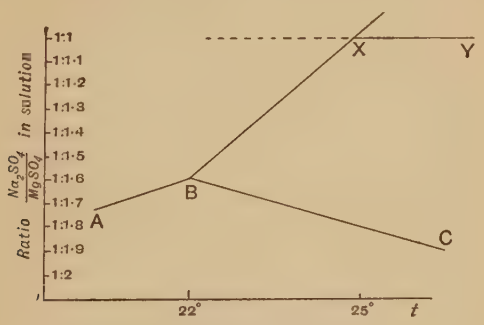


FIG. 115.

latter will therefore be deposited. From this, therefore, it is clear that if excess of astracanite is brought in contact with water at about the transition point, it will undergo decomposition with separation of Glauber's salt (supersaturation being excluded).

This will perhaps be made clearer by considering Fig. 115. In this diagram the ordinates represent the ratio of sodium sulphate to magnesium sulphate in the solutions, and the abcissæ represent the temperatures. The line AB represents solutions saturated with respect to a mixture of the single salts (p. 234) ; BC refers to solutions in

equilibrium with astracanite and magnesium sulphate; while BX represents the composition of solutions in contact with the solid phases astracanite and Glauber's salt. The values of the solubility are contained in the following table, and in that on p. 235, and are, as before, expressed in gm.-molecules of salt in 100 gm.-molecules of water:—[1]

Temperature.	Astracanite + sodium sulphate.		Astracanite + magnesium sulphate.	
	Na_2SO_4.	$MgSO_4$.	Na_2SO_4.	$MgSO_4$.
18·5°	—	—	3·41	4·27
22°	2·95	4·70	2·85	4·63
24·5°	3·45	3·62	2·68	4·76
30°	4·58	2·91	2·30	5·31
35°	4·30	2·76	1·73	5·88

At the transition point the ratio of sodium sulphate to magnesium sulphate is approximately 1 : 1·6. In the case of solutions saturated with respect to both astracanite and Glauber's salt, the relative amount of sodium sulphate increases as the temperature rises, while in the solutions saturated for astracanite and magnesium sulphate, the ratio of sodium sulphate to magnesium sulphate decreases.

If we consider only the temperatures above the transition point, we see from the figure that solutions represented by points above the line BX contain relatively more sodium sulphate than solutions in contact with astracanite and Glauber's salt; and solutions lying below the line BC contain relatively more magnesium sulphate than solutions saturated with this salt and astracanite. These solutions will therefore not be stable, but will deposit in the one case, astracanite and Glauber's salt, and in the other case, astracanite and magnesium sulphate, until a point on BX or BC is reached. All solutions, however, lying to the right of CBX, will be *unsaturated* with respect to these two pairs of salts, and only the solutions represented by the line XY (and which contain equimolecular amounts of sodium and magnesium sulphates) will be saturated with respect to the pure double salt.

Transition Interval.—Fig. 115 will also render intelligible a point of great importance in connection with astracanite, and with double salts generally. At temperatures between those represented by the points B and X, the double salt when brought in contact with water will be decomposed with separation of sodium sulphate. Above the temperature of the point X, however, the solution of the pure double salt is stable, because it can still take up a little of either of the components. At temperatures, then, above that at which the solution in contact with the double salt and the less soluble single salt, contains the single salts in the ratio in which they are present in the double salt,

[1] Roozeboom, *Z. physikal. Chem.*, 1888, **2**, 518.

solution of the latter will take place without decomposition. *The range of temperature between that at which double salt can begin to be formed (the transition point) and that at which it ceases to be decomposed by water is called the transition interval.*[1] If the two single salts have identical solubility at the transition point, the transition interval diminishes to nought.

In those cases where the double salt is the stable form below the transition point, the transition interval will extend downwards to a lower temperature. Fig. 115 will then have the reverse form.

Summary.—With regard to double salts we have learned that their formation from and their decomposition into the single salts is connected with a definite temperature, the *transition temperature*. At this transition temperature two vapour pressure curves cut, viz. a curve of dehydration of a mixture of the single salts and the solubility curve of the double salt; or the dehydration curve of the double salt and the solubility curve of the mixed single salts. The solubility curves, also, of these two systems intersect at the transition point, but although the formation of the double salt commences at the transition point, complete stability in contact with water may not be attained till some temperature above (or below) that point. *Only when the temperature is beyond the transition interval will a double salt dissolve in water without decomposition* (e.g. *the alums*).

[1] Meyerhoffer, *Z. physikal. Chem.*, 1890, **5**, 109. On the importance of the transition interval in the case of optically active substances, see Meyerhoffer, *Ber.*, 1904, **37**, 2604.

CHAPTER XV.

ISOTHERMAL CURVES AND THE SPACE MODEL.

In the preceding chapter we considered the changes in the solubility of double salts and of mixtures of their constituent salts with the temperature; noting, more especially, the relationships between the two systems at the transition point. It is now proposed to conclude the study of the three-component systems by discussing very briefly the solubility relations at constant temperature, or the isothermal solubility curves. In this way fresh light will be thrown on the change in the solubility of one component by the addition of another component, and also on the conditions of formation and stable existence of double salts in solution. With the help of these isothermal curves, also, the phenomena of crystallisation at constant temperature—phenomena which have not only a scientific interest but also an important bearing on the industrial preparation of double salts—will be more clearly understood.[1]

A brief description will also be given of the method of representing the variation of the concentration of the two salts in the solution with the temperature.

The Isothermal Diagram.—For the representation of the isothermal relations in a ternary system, various methods can be employed. One may, in the first place, employ the triangular diagram, the use of which has already been explained (p. 204). Where we are dealing with the equilibria between aqueous solutions and two salts with the same ion, a simple two-branched curve, *e.g. acb* (Fig. 116), will be obtained if the two salts do not form any double salt. In this diagram, *a* represents the solubility of the salt A, *b* the solubility of the salt B, while the curves *ac* and *bc* represent ternary solutions in equilibrium with solid salt A and solid salt B respectively. At *c* we have an invariant system in which the solution is in equilibrium with both salts as solid phases.

When the two components, A and B, can form a compound, the isothermal diagram will exhibit three curves, such as *ac*, *cc'*, *c'b* (Fig. 117), *c* and *c'* representing solutions which are in equilibrium with pure A and double salt, and pure B and double salt respectively. The composition of the anhydrous double salt is represented by the point D on the side of the triangle AB.

[1] In connection with this chapter, see, more especially, van't Hoff, *Bildung und Spaltung von Doppelsalzen*, pp. 3 ff.; Roozeboom, *Z. physikal. Chem.*, 1892, **10**, 158; Bancroft, *Phase Rule*, pp. 201, 209.

If the line joining the point D with the angle of the triangle representing pure water, cuts the curve *cc'* for the double salt (as in Fig. 117), then the double salt will be stable and will dissolve in water without undergoing decomposition (see *infra*, p. 244) ; but if the line joining D with the opposite angle of the triangle cuts the curve for one of the single salts, then the double salt on being brought into contact with water will undergo decomposition with deposition of the single salt.

A mixture of the three components having a total composition represented by a point *x* within the triangular area *a*A*c* (Fig. 116) will give rise to the heterogeneous system consisting of solid A and a saturated solution represented by the point on the saturation curve *ac* where the " tie-line " A*x* cuts the curve *ac*. Similarly, mixtures having a total composition represented by a point in the area *b*B*c* will give rise to solid B and a saturated solution represented by a point on the curve *bc*. From this diagram, also, the relative amounts of solid phase and saturated solution formed can be obtained. Thus, in the case of the

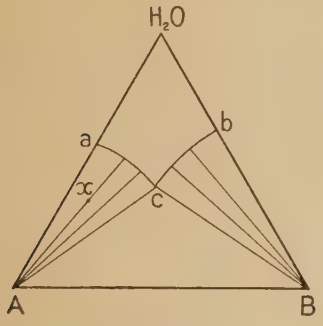


FIG. 116.

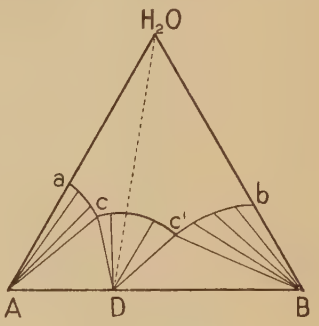


FIG. 117.

mixture *x*, the amount of saturated solution formed will be represented by the distance A*x*, and the amount of solid phase deposited will be represented by the distance of *x* from the curve *ac*.

Another method of representing the isothermal relations in a ternary system is by making use of the rectangular diagram due to Jänecke[1] (Fig. 118). In constructing this diagram the total salt is put equal to 100, and the amounts of the two salts, *x*A and (100 — *x*) B, are measured off along the side AB of the rectangle. The amount M of water in the solution associated with 100 parts of total salt, is measured upwards along the side of the rectangle. Since, according to this method, M would become infinite for pure water, it is better to represent the amount of water in the solution by a number N the value of which is given by $N = \frac{100\,M}{100 + M}$. For pure water ($M = \infty$), N becomes equal to 100.

[1] *Z. anorgan. Chem.*, 1906, **51**, 132.

A third method consists in representing the composition of the solutions in terms of grams or gram-molecules of each salt in a fixed amount (say 100 grams or 100 gram-molecules) of water. By this

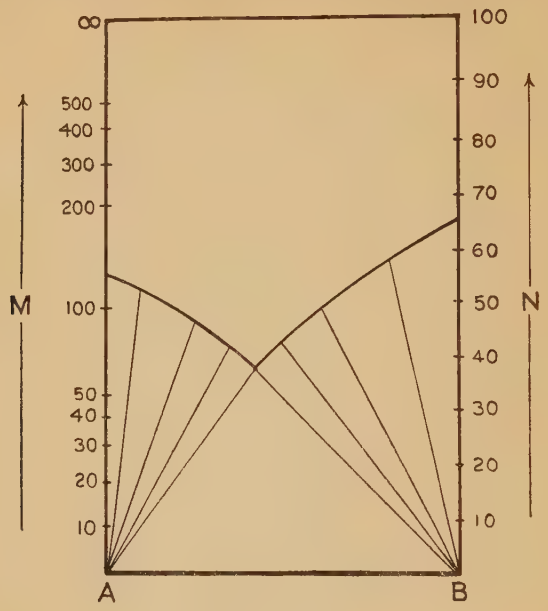


FIG. 118.

method one can make use of rectangular co-ordinates. In what follows we shall make use of this third method of representation.

Non-formation of Double Salts.—In Fig. 119 are shown the solubility curves of two salts, A and B, which at the given temperature do not form a double salt.[1] The ordinates represent the amount of A, the abscissæ the amount of B in a *constant amount* of the third component, the solvent. The point A, therefore, represents the solubility of the salt A at the given temperature; and similarly, point B represents the solubility of B. Since we are dealing with a three-component system, one solid phase in contact with solution will constitute a bi-variant system (in the absence of the vapour phase and under a constant pressure). At any given temperature, therefore, the concentration of the solution in equilibrium with the solid can undergo

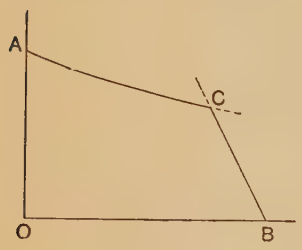


FIG. 119.

[1] The same restriction must be made here as was imposed in the preceding chapter, namely, that the two salts in solution give a common ion.

change. If to a pure solution of A a small quantity of B is added, the solubility of A will in general be altered; as a rule it is diminished, but sometimes it is increased.[1] The curve AC represents the varying composition of the solution in equilibrium with the solid component A. Similarly, the curve BC represents the composition of the solutions in contact with pure B as solid phase. At the point C, where these two curves intersect, there are two solid phases, viz. pure A and pure B, in equilibrium with solution, and the system becomes invariant. At this point the solution is saturated with respect to both A and B, and at a given temperature must have a perfectly definite composition. To take an example, if we suppose salt A to be sodium sulphate decahydrate, and salt B, magnesium sulphate heptahydrate, and if we assume the temperature to be 18·5°, then the point A (Fig. 119) will represent the solubility of sodium sulphate decahydrate at 18·5°; point B, the solubility of magnesium sulphate heptahydrate; and C, the composition of the solution in equilibrium with both salts as solid phases. This solution (p. 234) contains 2·16 gram-molecules Na_2SO_4 and 4·57 gram-molecules $MgSO_4$ per 100 gram-molecules of water.

The curve ACB is the boundary curve for saturated solutions. Solutions represented by a point lying within the area ACBO are unsaturated, whereas systems the composition of which is represented by points lying outside this area are either supersaturated solutions or mixtures of saturated solution and solid salt.

If from the point C lines be drawn, one upwards and parallel to OA and one to the right parallel to OB, three areas lying outside the equilibrium curve will be formed. Any point in the area based on AC will represent mixtures of solid A and saturated solutions of a composition represented by points on the curve AC; any point in the area to the right of BC will represent mixtures of solid B and saturated solutions represented by points on the curve BC; while a point in the intermediate area will represent a mixture of solid A and B, together with a saturated solution of the composition represented by C.

An equilibrium diagram of the type shown in Fig. 119 is also given by the system NaCl—KCl—H_2O.[2]

Formation of Double Salt.—We have already learned in the preceding chapter that if the temperature is outside[3] the transition interval, it is possible to prepare a pure saturated solution of the double salt. If we suppose the double salt to contain the two constituent salts in equimolecular proportions, its saturated solution must be represented by a point lying on the line which bisects the angle AOB; *e.g.*

[1] When the solubility of one salt is increased by the addition of another salt with a common ion, it may generally be inferred that compound formation takes place in the solution.

[2] Precht and Wittjen, *Ber.*, 1881, **14**, 1670; Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

[3] It must, of course, be understood that the temperature is on that side of the transition point on which the double salt is stable.

point D, Fig. 120. But a double salt constitutes only a single phase, and can exist, therefore, in contact with solutions of varying concentration, as represented by EDF.

Let us compare, now, the relations between the solubility curve for the double salt, and those for the two constituent salts. We shall suppose that the double salt is formed from the single salts when the temperature is raised above a certain point (as in the formation of astracanite). At a temperature below the transition point, as we have already seen, the solubility of the double salt is greater than that of a mixture of the single salts. The curve EDF, therefore, must lie above the point C, in the region representing solutions supersaturated with respect to the single salts (Fig. 121). Such a solution, however, would be metastable, and on being brought in contact with the single salts would deposit these and yield a solution represented by the point C. At this particular temperature, therefore, the isothermal solubility curve will consist of only two branches.

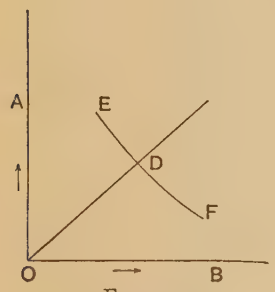


FIG. 120.

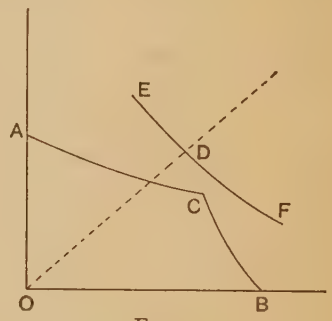


FIG. 121.

Suppose, now, that the temperature is that of the transition point. At this point, the double salt can exist together with the single salts in contact with solution. The solubility curve of the double salt must, therefore, pass through the point C, as shown in Fig. 122.

From this figure it is seen that a solution saturated with respect to double salt alone (point D), is supersaturated with respect to the component A. If, then, at the temperature of the transition point, excess of the double salt is brought in contact with water,[1] and if supersaturation is excluded, *the double salt will undergo decomposition and the component A will be deposited.* The relative concentration of the component B in the solution will, therefore, increase, and the composition of the solution will be thereby altered in the direction DC. When the solution has the composition of C, the single salt ceases to be deposited, for at this point the solution is saturated for both double and single salt; and the system becomes invariant.

[1] Excess of the double salt must be taken, because otherwise an unsaturated solution might be formed, and this would, of course, not deposit any salt.

This diagram explains very clearly the phenomenon of the decomposition of a double salt at the transition point. As is evident, this decomposition will occur when the solution which is saturated at the temperature of the transition point, with respect to the two single salts (point C), does not contain these salts in the same ratio in which they are present in the double salt. If point C lay on the dotted line bisecting the right angle, then the pure saturated solution of the double salt would not be supersaturated with respect to either of the single salts, and the double salt would, therefore, not be decomposed by water. As has already been mentioned, this behaviour is found in the case of optically active isomerides, the solubilities of which are identical.

At the transition point, therefore, the isothermal curve also consists of two branches; but the point of intersection of the two branches now represents a solution which is saturated not only with respect to the single salts, but also for the double salt in presence of the single salts.

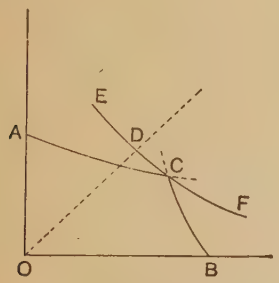


FIG. 122.

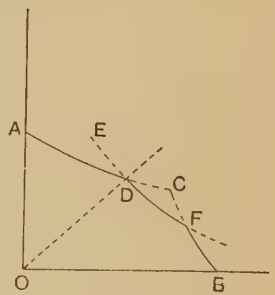


FIG. 123.

We have just seen that by a change of temperature the two solubility curves, that for the two single salts and that for the double salt, were made to approach each other (*cf.* Figs. 121 and 122). In the previous chapter, however, we found that on passing the transition point to the region of stability for the double salt, the solution which is saturated for a mixture of the two constituent salts is supersaturated for the double salt. In this case, therefore, point C must lie above the solubility curve of the pure double salt (Fig. 123), and a solution of the composition C, if brought in contact with double salt, will deposit the latter. If the single salts were also present, then as the double salt separated out, the single salts would pass into solution, because so long as the two single salts are present, the composition of the solution must remain unaltered. If one of the single salts disappear before the other, there will be left double salt plus A, or double salt plus B, according to which was in excess; and the composition of the solution will be either that represented by D (saturated for double salt plus A), or that of the point F (saturated for double salt plus B).

In connection with the isothermal represented in Fig. 123, it should be noted that at this particular temperature a solution saturated with respect to the pure double salt is no longer supersaturated for one of the single salts (point D); so that at the temperature of this isothermal the double salt is not decomposed by water. At this temperature, further, the boundary curve consists of three branches—AD, DF, and FB—which give the composition of the solutions in equilibrium with pure A, double salt, and pure B respectively; while the points D and F represent solutions saturated for double salt plus A and double salt plus B.

On continuing to alter the temperature in the same direction as before, the relative shifting of the solubility curves becomes more marked, as shown in Fig. 124. At the temperature of this isothermal, the solution saturated for the double salt now lies in a region of distinct unsaturation with respect to the single salts; and the double salt can now exist as solid phase in contact with solutions containing both relatively more of A (curve ED), and relatively more of B (curve DF), than is contained in the double salt itself.

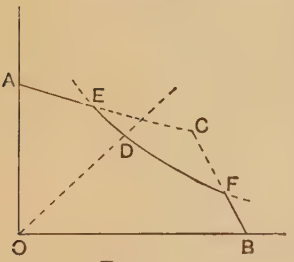


FIG. 124.

Transition Interval.—From what has been said, and from an examination of the isothermal diagrams (Figs. 121-124), it will be seen that by a variation of the temperature we can pass from a condition where the double salt is quite incapable of existing in contact with solution (supersaturation being excluded), to a condition where the existence of the double salt in presence of solution becomes possible; only in the presence, however, of one of the single salts (*transition point*, Fig. 122). A further change of temperature leads to a condition where the stable existence of the pure double salt in contact with solution just becomes possible (Fig. 123); and from this point onwards, pure saturated solutions of the double salt can be obtained (Fig. 124). *At any temperature, therefore, between that represented by Fig.* 122, *and that represented by Fig.* 123, *the double salt undergoes partial decomposition, with deposition of one of the constituent salts.* The temperature range between the transition point and the temperature at which a stable saturated solution of the pure double salt just begins to be possible, is known as the *transition interval* (p. 236). As the figures show, the transition interval is limited on the one side by the transition temperature, and on the other by the temperature at which the solution saturated for double salt and the less soluble of the single salts contains the component salts in the same ratio as they are present in the double salt. The greater the difference in the solubility of the single salts, the larger will be the transition interval.

Isothermal Evaporation.—The isothermal solubility curves are of great importance for obtaining an insight into the behaviour of a solu-

tion when subjected to isothermal evaporation. To simplify the discussion of the relationships found here, we shall still suppose that the double salt contains the single salts in equimolecular proportions; and we shall, in the first instance, suppose that the unsaturated solution with which we commence, also contains the single salts in the same ratio. The composition of the solution must, therefore, be represented by some point lying on the line OD, the bisectrix of the right angle.

From what has been said, it is evident that when the formation of a double salt can occur, three temperature intervals can be distinguished, viz. the single-salt interval, the transition interval, and the double-salt interval.[1] When the temperature lies in the first interval, evaporation leads first of all to the crystallisation of one of the single salts, and then to the separation of both the single salts together. In the second temperature interval, evaporation again leads, in the first place, to the deposition of one of the single salts, and afterwards to the crystallisation of the double salt. In the third temperature interval, only the double salt crystallises out. This will become clearer from what follows.

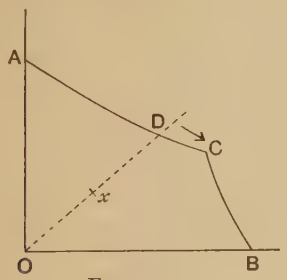


FIG. 125.

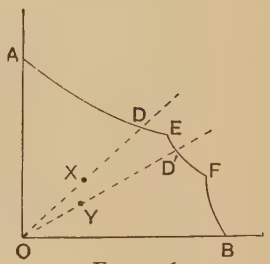


FIG. 126.

If an unsaturated solution of the two single salts in equimolecular proportion (*e.g.* point *x*, Fig. 125) is evaporated at a temperature at which the formation of double salt is impossible, the component A, the solubility curve of which is cut by the line OD, will first separate out; the solution will thereby become richer in B. On continued evaporation, more A will be deposited, and the composition of the solution will change, as shown by the arrow, until it attains the composition represented by the point C, when both A and B will be deposited, and the composition of the solution will remain unchanged. The result of evaporation will therefore be a mixture of the two components.

If the formation of double salt is possible, but if the temperature lies within the transition interval, the relations will be represented by a diagram like Fig. 126. Isothermal evaporation of the solution X will lead to the deposition of the component A, and the composition of the solution will alter in the direction DE; at the point E, the double salt will be formed, and the composition of the solution will remain

[1] Meyerhoffer, *Ber.*, 1904, 37, 2605.

unchanged so long as the two solid phases are present. As can be seen from the diagram, however, the solution in E contains less of component A than is contained in the double salt. Deposition of the double salt at E, therefore, would lead to a relative decrease in the concentration of A in the solution, and to counterbalance this, *the salt which separated out at the commencement must redissolve.*

Since the salts were originally present in equimolecular proportions, the final result of evaporation will be the pure double salt. If when the solution has reached the point E the salt A which had separated out is removed, double salt only will be left as solid phase. At a given temperature, however, a single solid phase can exist in equilibrium with solutions of different composition. If, therefore, isothermal evaporation is continued after the removal of the salt A, double salt will be deposited, and the composition of the solution will change in the direction EF. At the point F the salt B will separate out, and on evaporation both double salt and the salt B will be deposited. In the former case (when the salt A disappears on evaporation) we are dealing with an *incongruently saturated solution ;* but in the latter case, where both solid phases continue to be deposited, the solution is said to be *congruently saturated.*[1]

A " congruently saturated solution " is one from which the solid phases are continuously deposited during isothermal evaporation to dryness, whereas in the case of " incongruently saturated solutions," at least one of the solid phases disappears during the process of evaporation.

Lastly, if the temperature lies outside the transition interval, isothermal evaporation of an unsaturated solution of the composition X (Fig. 127) will lead to the deposition of pure double salt from beginning to end. If a solution of the composition Y is evaporated, the component A will first be deposited and the composition of the solution will alter in the direction of E, at which point double salt will separate out. Since the solution at this point contains relatively more of A than is present in the double salt, both the double salt and the single salt A will be deposited on continued evaporation, in order that the composition of the solution shall remain unchanged. In the case of solution Z, first component B and afterwards the double salt will be deposited. The result will, therefore, be a mixture of double salt and the salt B (congruently saturated solutions).

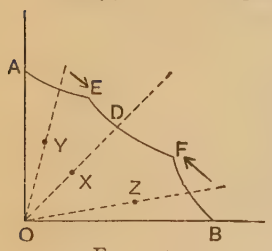


FIG. 127.

It may be stated here that the same relationships as have been explained above for double salts are also found in the resolution of racemic compounds by means of optically active substances (third method of Pasteur). In this case the single salts are doubly active

[1] Meyerhoffer, *Ber.*, 1897, **30**, 1809.

substances (*e.g.* strychnine-*d*-tartrate and strychnine-*l*-tartrate), and the double salt is a partially racemic compound.[1]

Crystallisation of Double Salt from Solutions containing Excess of One Component.—One more case of isothermal crystallisation may be discussed. It is well known that a double salt which is decomposed by pure water can nevertheless be obtained pure by crystallisation from a solution containing excess of one of the single salts (*e.g.* in the case of carnallite). Since the double salt is partially decomposed by water, the temperature of the experiment must be within the transition interval, and the relations will, therefore, be represented by a diagram like Fig. 126. If, instead of starting with an unsaturated solution containing the single salts in equimolecular proportions, we commence with one in which excess of one of the salts is present, as represented by the point Y, isothermal evaporation will cause the composition to alter in the direction YD′, the relative amounts of the single salts remaining the same throughout. When the composition of the solution reaches the point D′, pure double salt will be deposited. The separation of double salt will, however, cause a relative decrease in the concentration of the salt A, and the composition of the solution will, therefore, alter in the direction D′F. If the evaporation is discontinued before the solution has attained the composition F, only double salt will have separated out. Even within the transition interval, therefore, pure double salt can be obtained by crystallisation, provided the original solution has a composition represented by a point lying between the two lines OE and OF. Since, as already shown, the composition of the solution alters on evaporation in the direction EF, it will be best to employ a solution having a composition near to the line OE.

Formation of Mixed Crystals or Solid Solutions.—If the two single salts A and B do not crystallise out pure from solution, but form an unbroken series of mixed crystals (solid solutions), it is evident that an invariant system cannot be produced. The solubility curve will therefore be continuous from A to B, the liquid solutions of varying composition being in equilibrium with solid solutions also of varying composition. If, however, the series of mixed crystals is not continuous, there will be a break in the solubility curve at which two solid solutions of different composition will be in equilibrium with liquid solution. This, of course, will constitute an invariant system, and the point will correspond to the point C in Fig. 125. A full discussion of these systems would, however, lead us too far, and the above indication of the behaviour must suffice.[2]

[1] Meyerhoffer, *Ber.*, 1904, **37**, 2604. See also footnote, p. 249.

[2] Bancroft, *Phase Rule*, p. 203; Roozeboom, *Z. physikal. Chem.*, 1891, **8**, 504, 531; Stortenbeker, *ibid.*, 1895, **17**, 643; 1897, **22**, 60; 1900, **34**, 108. See also experimental investigations by Allmand, *Z. anorgan. Chem.*, 1909, **61**, 202; Clendinnen and Rivett, *J. Chem. Soc.*, 1921, **119**, 1329; 1923, **123**, 1344, 1634; Perman and Howells, *ibid.*, 1923, **123**, 2128. See also the monograph by Blasdale, *Equilibria in Saturated Salt Solutions* (Chemical Catalog Co.), where the subject is fully discussed.

Application to the Characterisation of Racemates.—The form of the isothermal solubility curves is also of great value for determining whether an inactive substance is a racemic compound or a conglomerate of equal proportions of the optical antipodes.[1]

As has already been pointed out, the formation of racemic compounds from the two enantiomorphous isomerides, is analogous to the formation of double salts. The isothermal solubility curves also have a similar form. In the case of the latter, indeed, the relationships are simplified by the fact that the two enantiomorphous forms have identical solubility, and the solubility curves are therefore symmetrical to the line bisecting the angle of the co-ordinates. Further, with the exception of the partially racemic compounds to be mentioned later, there is no transition interval.

In Fig. 128 are given diagrammatically two isothermal solubility curves for optically active substances. From what has been said in the immediately preceding pages, the figure ought really to explain itself. The upper isothermal *acb* represents the solubility relations

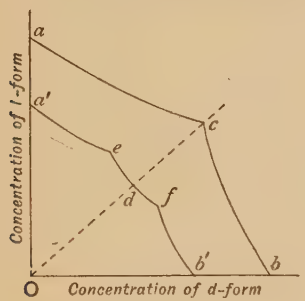


FIG. 128.

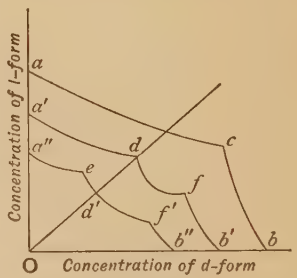


FIG. 129.

when the formation of a racemic compound is excluded, as, *e.g.* in the case of rubidium *d*- and *l*-tartrates above the transition point (p. 233). The solution at the point *c* is, of course, inactive, and *is unaffected by addition of either the* d- *or* l-*form*. The lower-isothermal, on the other hand, would be obtained at a temperature at which the racemic compound could be formed. The curve *a'e* is the solubility curve for the *l*-form; *b'f*, that for the *d*-form; and *edf*, that for the racemic compound in presence of solutions of varying concentration. The point *d* corresponds to saturation for the pure racemic compound.

From these curves, now, it will be evident that it will be possible, in any given case, to decide whether or not an inactive solid is a mixture or a racemic compound. For this purpose, two solubility determinations are made, first with the inactive material alone (in excess), and then with the inactive material plus excess of one of the optically active forms. If we are dealing with a mixture, the two solutions thus obtained will be identical; both will have the composition corre-

[1] Roozeboom, *Z. physikal. Chem.*, 1899, **28**, 494; *Ber.*, 1899, **32**, 537.

sponding to the point *c*, and will be inactive. If, however, the inactive material is a racemic compound, then two different solutions will be obtained; namely, an inactive solution corresponding to the point *d* (Fig. 128), and an *active* solution corresponding either to *e* or to *f*, according to which enantiomorphous form was added.

Partially racemic compounds.[1]—In this case we are no longer dealing with enantiomorphous forms, and the solubility of the two oppositely active isomerides is no longer the same. The symmetry of the solubility curves therefore disappears, and a figure is obtained which is identical in its general form with that found in the case of ordinary double salts (Fig. 129). In this case there is a transition interval.

The curves *acb* belong to a temperature at which the partially racemic compound cannot be formed; *a'dfb'*, to the temperature at which the compound just begins to be stable in contact with water, and *a''ed'f'b''* belongs to a temperature at which the partially racemic compound is quite stable in contact with water. Suppose solubility determinations made, in the first case, with the original material alone, and then with the original body plus each of the two compounds, formed from the enantiomorphous substances separately, then if the original body was a mixture, identical solutions will be obtained in all three cases (point *c*); if it was a partially racemic compound, three different solutions (*e*, *d'*, *f'*) will be obtained if the temperature was outside the transition interval, and two solutions, *d* and *f*, if the temperature belonged to the transition interval.

Representation in Space.

Space Model for Carnallite.—Interesting and important as the isothermal solubility curves are, they are insufficient for the purpose of obtaining a clear insight into the complete behaviour of the systems of two salts and water. A short description will, therefore, be given here of the representation in space of the solubility relations of potassium and magnesium chlorides, and of the double salt which they form, carnallite.[2]

Fig. 130 is a diagrammatic sketch of the model for carnallite looked at sideways from above. Along the X-axis is measured the concentration of magnesium chloride in the solution; along the Y-axis, the concentration of potassium chloride; while along the T-axis is

[1] As, for instance, strychnine racemate, a compound of racemic acid with the *optically active* strychnine. This would be resolved into strychnine *d*-tartrate and strychnine *l*-tartrate, which are not enantiomorphous forms. This behaviour has been investigated in the case of the *l*-menthyl ester of the mandelic acids (Findlay and Hickmans, *J. Chem. Soc.*, 1907, **91**, 905. See also H. Dutilh, *Proc. K. Akad. Wetensch. Amsterdam*, 1909, **12**, 393).

[2] Van't Hoff and Meyerhoffer, *Z. physikal. Chem.*, 1898, **27**, 75; 1899, **30**, 86; Fig. 130 is taken from the latter paper. See also Jänecke, *Z. anorgan. Chem.*, 1906, **51**, 128; Freeth, *Phil. Trans.*, 1923, **223**, A, 37. To facilitate the understanding of the space models, the reader is referred to Kremann's *Leitfaden der graphischen Chemie* (Borntraeger), which gives instructions and materials for making cardboard models of different systems.

measured the temperature. The three axes are at right angles to one another. The XT-plane, therefore, contains the solubility curve of magnesium chloride; the YT-plane, the solubility curve of potassium chloride, and in the space between the two planes, there are represented the composition of solutions containing both magnesium and potassium chlorides. Any *surface* between the two planes will represent the various solutions in equilibrium with only one solid phase, and will therefore indicate the area or field of existence of bivariant ternary systems. A *line* or *curve* formed by the intersection of two surfaces will represent solutions in equilibrium with two solid

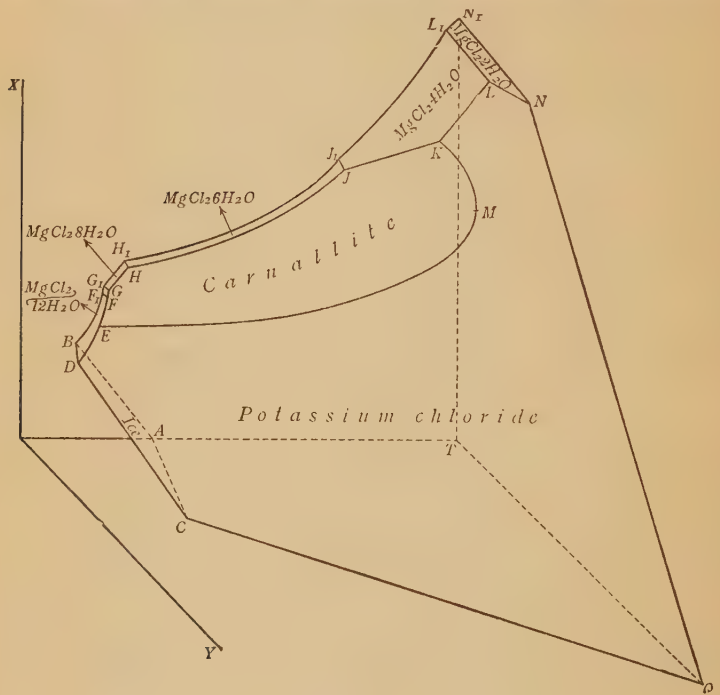


Fig. 130.

phases (viz. those belonging to the intersecting surfaces), and will show the conditions for the existence of univariant systems. Lastly, *points* formed by the intersection of three surfaces will represent invariant systems, in which a solution can exist in equilibrium with three solid phases (viz. those belonging to the three surfaces).

We shall first consider the solubility relations of the single salts. The complete equilibrium curve for magnesium chloride and water is represented in Fig. 130 by the series of curves $ABF_1G_1H_1J_1L_1N_1$. AB is the freezing-point curve of ice in contact with solutions containing magnesium chloride, and B is the cryohydric point at which the solid

phases ice and $MgCl_2,12H_2O$ can coexist with solution. BF_1G_1 is the solubility curve of magnesium chloride dodecahydrate. This curve shows a point of maximum temperature at F_1, and a retroflex portion F_1G_1. The curve is therefore of the form exhibited by calcium chloride hexahydrate, or the hydrates of ferric chloride (Chapter XI.). G_1 is a transition point at which the solid phase changes from dodecahydrate to octahydrate, the solubility of which is represented by the curve G_1H_1. At H_1 the octahydrate gives place to the hexahydrate, which is the solid phase in equilibrium with the solutions represented by the curve H_1J_1. J_1 and L_1 are also transition points at which the solid phase undergoes change, in the former case from hexahydrate to tetrahydrate, and in the latter case from tetrahydrate to dihydrate. The complete curve of equilibrium for magnesium chloride and water is, therefore, somewhat complicated, and is a good example of the solubility curves obtained with salts capable of forming several hydrates.

The equilibrium curve for potassium chloride and water is of the simplest form, consisting only of the two branches AC, the freezing-point curve of water, and CO, the solubility curve of the salt. C is the cryohydric point. This point and the two curves lie in the YT-plane.

On passing to the ternary systems, the composition of the solutions must be represented by points or curves situated *between* the two planes. We shall now turn to the consideration of these. BD and CD are ternary eutectic curves (p. 220). They give the composition of solutions in equilibrium with ice and magnesium chloride dodecahydrate (BD), and with ice and potassium chloride (CD). D is a *ternary cryohydric point.* If the temperature is raised and the ice allowed to disappear, we shall pass to the solubility curve for $MgCl_2,12H_2O + KCl$ (curve DE). At E carnallite is formed and the potassium chloride disappears; EFG is then the solubility curve for $MgCl_2,12H_2O$ + carnallite ($KMgCl_36H_2O$). This curve also shows a point of maximum temperature (F) and a retroflex portion. GH and HJ represent the solubility curves of carnallite + $MgCl_2,8H_2O$ and carnallite + $MgCl_2,6H_2O$, G and H being transition points. JK is the solubility curve for carnallite + $MgCl_2,4H_2O$. At the point K we have the *highest temperature at which carnallite can exist with magnesium chloride in contact with solution.* Above this temperature decomposition takes place and potassium chloride separates out.

If at the point E, at which the two single salts and the double salt are present, excess of potassium chloride is added, the magnesium chloride will all disappear owing to the formation of carnallite, and there will be left carnallite and potassium chloride. The solubility curve for a mixture of these two salts is represented by EMK; a simple curve exhibiting, however, a temperature maximum at M. This maximum point corresponds with the fact that dry carnallite melts at this temperature with separation of potassium chloride. *At all temperatures above this point, the formation of double salt is impossible.*

The retroflex portion of the curve represents solutions in equilibrium with carnallite and potassium chloride, but in which the ratio $MgCl_2 : KCl$ is greater than in the double salt.

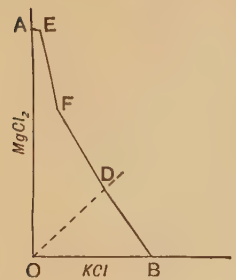


FIG. 131.

Throughout its whole course, *the curve EMK represents solutions in which the ratio of $MgCl_2 : KCl$ is greater than in the double salt.* As this is a point of some importance, it will be well, perhaps, to make it clearer by giving one of the isothermal curves, *e.g.* the curve for 10°, which is represented diagrammatically in Fig. 131. E and F here represent solutions saturated for carnallite plus magnesium chloride hydrate, and for carnallite plus potassium chloride. As is evident, the point F lies above the line representing equimolecular proportions of the salts (OD).

Summary and Numerical Data.—We may now sum up the different systems which can be formed, and give the numerical data from which the model is constructed.[1]

With the help of the data in the table on page 253 and of the solid model it will be possible to state in any given case what will be the behaviour of a system composed of magnesium chloride, potassium chloride and water. One or two different cases will be very briefly described; and the reader should have no difficulty in working out the behaviour under other conditions with the help of the model and the numerical data given.

In the first place, it may be again noted that at a temperature above 167·5° (point M) carnallite cannot exist. If, therefore, a solution of magnesium and potassium chlorides is evaporated at a temperature above this point, the result will be a mixture of potassium chloride and either magnesium chloride tetrahydrate or magnesium chloride dihydrate, according as the temperature is below or above 176°. The isothermal curve here consists of only two branches.

Further, reference has already been made to the fact that all points of the carnallite area correspond to solutions in equilibrium with carnallite, but in which the ratio of $MgCl_2$ to KCl is greater than in the double salt. A solution which is saturated with respect to double salt alone will be supersaturated with respect to potassium chloride. At all temperatures, therefore, carnallite is decomposed by water with separation of potassium chloride; hence all solutions obtained by adding excess of carnallite to water will lie on the curve EM. *A pure saturated solution of carnallite cannot be obtained.*

If an unsaturated solution of the two salts in equimolecular amounts is evaporated, potassium chloride will first be deposited, because the plane bisecting the right angle formed by the X and Y axes cuts the

[1] Solid models constructed of plaster of Paris can be obtained from Max Kaehler and Martini, Berlin.

I. *Bivariant Systems.*

Solid phase.	Area of existence.
Ice	ABDC
KCl	CDEMKLNO
Carnallite	EFGHJKM
$MgCl_2,12H_2O$	BF_1G_1GFED
$MgCl_2,8H_2O$	G_1H_1HG
$MgCl_2,6H_2O$	H_1I_1IH
$MgCl_2,4H_2O$	I_1L_1LKI
$MgCl_2,2H_2O$	L_1N_1NL

II. *Univariant Systems.*—The different univariant systems have already been described. The course of the curves will be sufficiently indicated if the temperature and composition of the solutions for the different invariant systems are given.

III. *Invariant Systems—Binary and Ternary.*

Point.	Solid phases.	Temperature.	Composition of solution. Gram-molecules of salt per 1000 gram-mol. water.
A	Ice	0°	—
B	Ice; $MgCl_2,12H_2O$	− 33·6°	49·2 $MgCl_2$
C	Ice; KCl	− 11·1°	59·4 KCl
D	Ice; $MgCl_2,12H_2O$; KCl	− 34·3°	43 $MgCl_2$; 3KCl
E	$MgCl_2,12H_2O$; KCl; carnallite	− 21°	66·1 $MgCl_2$; 4·9 KCl
F_1	$MgCl_2,12H_2O$	− 16·4°	83·33 $MgCl_2$
F	$MgCl_2,12H_2O$; carnallite	− 16·6°	Almost same as F; contains small amount of KCl
G_1	$MgCl_2,12H_2O$; $MgCl_2,8H_2O$	− 16·8°	87·5 $MgCl_2$
G	$MgCl_2,12H_2O$; $MgCl_2,8H_2O$; carnallite	− 16·9°	Almost same as G_1, but contains small quantity of KCl
H_1	$MgCl_2,8H_2O$; $MgCl_2,6H_2O$	− 3·4°	99 $MgCl_2$
H	$MgCl_2,8H_2O$; $MgCl_2,6H_2O$; carnallite	ca. − 3·4°	Almost same as H_1, but contains small amount of KCl
J_1	$MgCl_2,6H_2O$; $MgCl_2,4H_2O$	116·67°	161·8 $MgCl_2$
J	$MgCl_2,6H_2O$ $MgCl_2,4H_2O$; carnallite	115·7°	162 $MgCl_2$; 4 KCl
K	$MgCl_2,4H_2O$; KCl; carnallite	152·5°	200 $MgCl_2$; 24 KCl
L_1	$MgCl_2,4H_2O$; $MgCl_2,2H_2O$	181°	238·1 $MgCl_2$
L	$MgCl_2,4H_2O$; $MgCl_2,2H_2O$; KCl	176°	240 $MgCl_2$; 41 KCl
M	Carnallite; KCl	167·5°	166·7 $MgCl_2$; 41·7 KCl
[N_1	$MgCl_2,2H_2O$	186°	ca. 241 $MgCl_2$]
N	$MgCl_2,2H_2O$; KCl	186°	240 $MgCl_2$; 63 KCl
[O	KCl	186°	195·6 KCl]

area for that salt. Deposition of potassium chloride will lead to a relative increase in the concentration of magnesium chloride in the solution; and on continued evaporation a point (on the curve EM) will be reached at which carnallite will separate out. So long as the two solid phases are present, the composition of the solution must remain unchanged. Since the separation of carnallite causes a decrease in the relative concentration of the potassium chloride in the solution, the portion of this salt which was deposited at the commencement must *redissolve*, and carnallite will be left on evaporating to dryness. (*Incongruently saturated solution.*)

Although carnallite is decomposed by pure water, it will be possible to crystallise it from a solution having a composition represented by any point in the carnallite area. Since during the separation of the double salt the relative amount of magnesium chloride increases, it is most advantageous to commence with a solution the composition of which is represented by a point lying just above the curve EM (*cf.* p. 247).

From the above description of the behaviour of carnallite in solution, the processes usually employed for obtaining potassium chloride will be readily intelligible.[1]

Ferric Chloride—Hydrogen Chloride—Water.—In the case of another system of three components which we shall now describe, the relationships are considerably more complicated than in those already discussed. They deserve discussion, however, on account of the fact that they exhibit a number of new phenomena.

In the system formed by the three components, ferric chloride, hydrogen chloride and water, not only can various compounds of ferric chloride and water (p. 187) and of hydrogen chloride and water be formed, each of which possesses a definite melting-point, but various ternary compounds are also known. Thus we have the following solid phases :—

$2FeCl_3,12H_2O$	$HCl,3H_2O$	$2FeCl_3,2HCl,12H_2O$
$2FeCl_3,7H_2O$	$HCl,2H_2O$	$2FeCl_3,2HCl,8H_2O$
$2FeCl_3,5H_2O$	HCl,H_2O	$2FeCl_3,2HCl,4H_2O$
$2FeCl_3,4H_2O$		
$FeCl_3$		

From this it will be readily understood that the complete study of the conditions of temperature and concentration under which solutions can exist, either with one solid phase or with two or three solid phases, are exceedingly complicated; and, as a matter of fact, only a few of the possible equilibria have been investigated. We shall attempt here only a brief description of the most important of these.[2]

If we again employ rectangular co-ordinates for the graphic repre-

[1] Instead of the present method of obtaining potassium chloride by decomposing carnallite with water, advantage might be taken of the fact that carnallite when heated to 168° undergoes decomposition with separation of three-fourths of the potassium chloride (van't Hoff, *Acht Vorträge über physikalische Chemie*, 1902, p. 32).

[2] Roozeboom and Schreinemakers, *Z. physikal. Chem.*, 1894, **15**, 588.

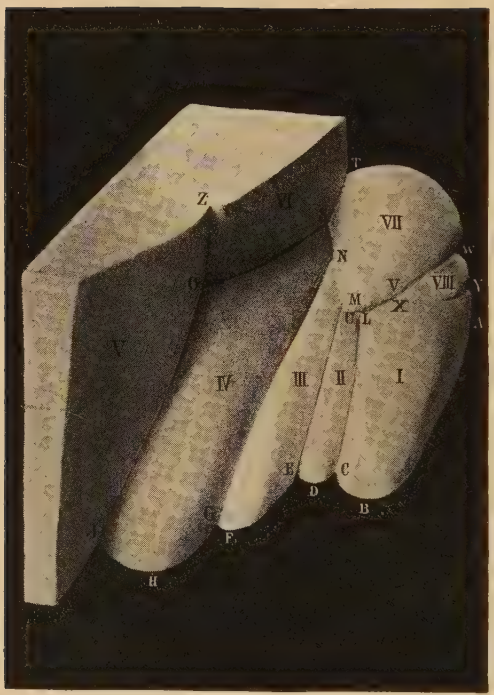


FIG. 133.—Model of systems of $FeCl_3$—HCl—H_2O.

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sentation of the results, we have the two planes XOT and YOT (Fig. 132): the concentration of ferric chloride being measured along the X-axis, the concentration of hydrogen chloride along the Y-axis, and the temperature along the T-axis. The curve ABCDEFGHJK is, therefore, the solubility curve of ferric chloride in water (p. 187), and the curve A′B′C′D′E′F′ the solubility curve of hydrogen chloride and its hydrates. B′ and D′ are the melting-points of the hydrates $HCl,3H_2O$ and $HCl,2H_2O$. In the space between these two planes are represented those systems in which all three components are present. As already stated, only a few of the possible ternary systems have been investigated, and these are represented in Fig. 133. The figure shows the model resting on the XOT-plane, so that the lower edge represents the solubility curve of ferric chloride, the concentration increasing from right to left. The concentration of hydrogen chloride is measured upwards, and the temperature forwards. The farther end of the model represents the isothermal surface for — 30°. The surface of the model on the left does not correspond with the plane YOT in Fig. 132, but with a parallel plane which cuts the concentration axis for ferric chloride at a point representing 65 gram-molecules $FeCl_3$ in 100 gram-molecules of water. The upper surface corresponds with a plane parallel to the axis XOT, at a distance corresponding with the concentration of 50 gram-molecules HCl in 100 gram-molecules of water.

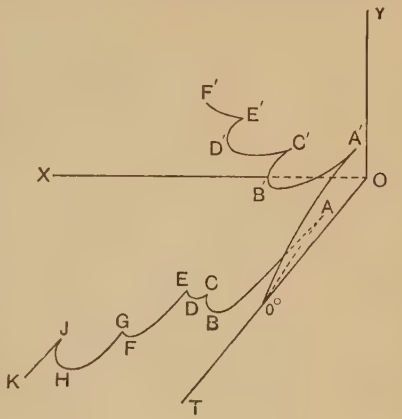

FIG. 132.

Ternary Systems.—We pass over the binary system $FeCl_3$—H_2O, which has already been discussed (p. 187), and the similar system HCl—H_2O (see Fig. 132), and turn to the discussion of some of the ternary systems represented by points on the surface of the model between the planes XOT and YOT. As in the case of carnallite, a plane represents the conditions of concentration of solution and temperature under which a ternary solution can be in equilibrium with a *single* solid phase (bivariant systems), a line represents the conditions for the co-existence of a solution with two solid phases (univariant systems), and a point the conditions for equilibrium with three solid phases (invariant systems).

In the case of a binary system, in which $2FeCl_3,12H_2O$ is in equilibrium with a solution of the same composition, addition of hydrogen chloride must evidently lower the temperature at which equilibrium can exist; and the same holds, of course, for all other binary solutions

in equilibrium with this solid phase. In this way we obtain the surface I., which represents the temperatures and concentrations of solutions in which $2FeCl_3,12H_2O$ can be in equilibrium with a ternary solution containing ferric chloride, hydrogen chloride, and water. This surface is analogous to the curved surface $K_1K_2k_4k_3$ in Fig. 104 (p. 220). Similarly, the surfaces II., III., IV., and V represent the conditions for equilibrium between the solid phases $2FeCl_3,7H_2O$; $2FeCl_3,5H_2O$; $2FeCl_3,4H_2O$; $FeCl_3$ and ternary solutions respectively. The lines CL, EM, GN, and IO on the model represent univariant systems in which a ternary solution is in equilibrium with two solid phases, viz. with those represented by the adjoining fields. These lines correspond with the ternary eutectic curves k_3K_1 and k_4K_2 in Fig. 104. Besides the surfaces already mentioned, there are still three others, VI., VII., and VIII., which also represent the conditions for equilibrium between one solid phase and a ternary solution; but in these cases, the solid phase is not a binary compound or an anhydrous salt, but a ternary compound containing all three components. The solid phases which are in equilibrium with the ternary solutions represented by the surfaces VI., VII., and VIII., are $2FeCl_3,2HCl,4H_2O$; $2FeCl_3,2HCl,8H_2O$; and $2FeCl_3,2HCl,12H_2O$ respectively.

The model for $FeCl_3$—HCl—H_2O exhibits certain other peculiarities not found in the case of $MgCl_2$—KCl—H_2O. On examining the model more closely, it is found that the field of the ternary compound $2FeCl_3,2HCl,8H_2O$ (VII.) resembles the surface of a sugar cone, and has a projecting point, the end of which corresponds with a higher temperature than does any other point of the surface. At the point of maximum temperature the composition of the liquid phase is the same as that of the solid. This point, therefore, represents the melting-point of the double salt of the above composition.

The curves representing univariant systems are of two kinds. In the one case, the two solid phases present are both binary compounds; or one is a binary compound and the other is one of the components. In the other case, either one or both solid phases are ternary compounds. Curves belonging to the former class (so-called *border curves*) start from binary eutectic points, and their course is always towards lower temperatures, *e.g.* CL, EM, GN, IO. Curves belonging to the latter class (so-called *medial curves*) would, in a triangular diagram, lie entirely within the triangle. Such curves are YV, WV, VL, LM, MV, NS, ST, SO, OZ. These curves do not always run from higher to lower temperatures, but may even exhibit a point of maximum temperature. Such maxima are found, for example, at U (Fig. 133), and also on the curves ST and LV.

Finally, whereas all the other ternary univariant curves run in valleys between the adjoining surfaces, we find at the point X a similar appearance to that found in the case of carnallite, as the univariant curve here rises above the surrounding surface. The point X, therefore, does not correspond with a eutectic point, but with a transition point. At this point the ternary compound $2FeCl_3,2HCl,12H_2O$

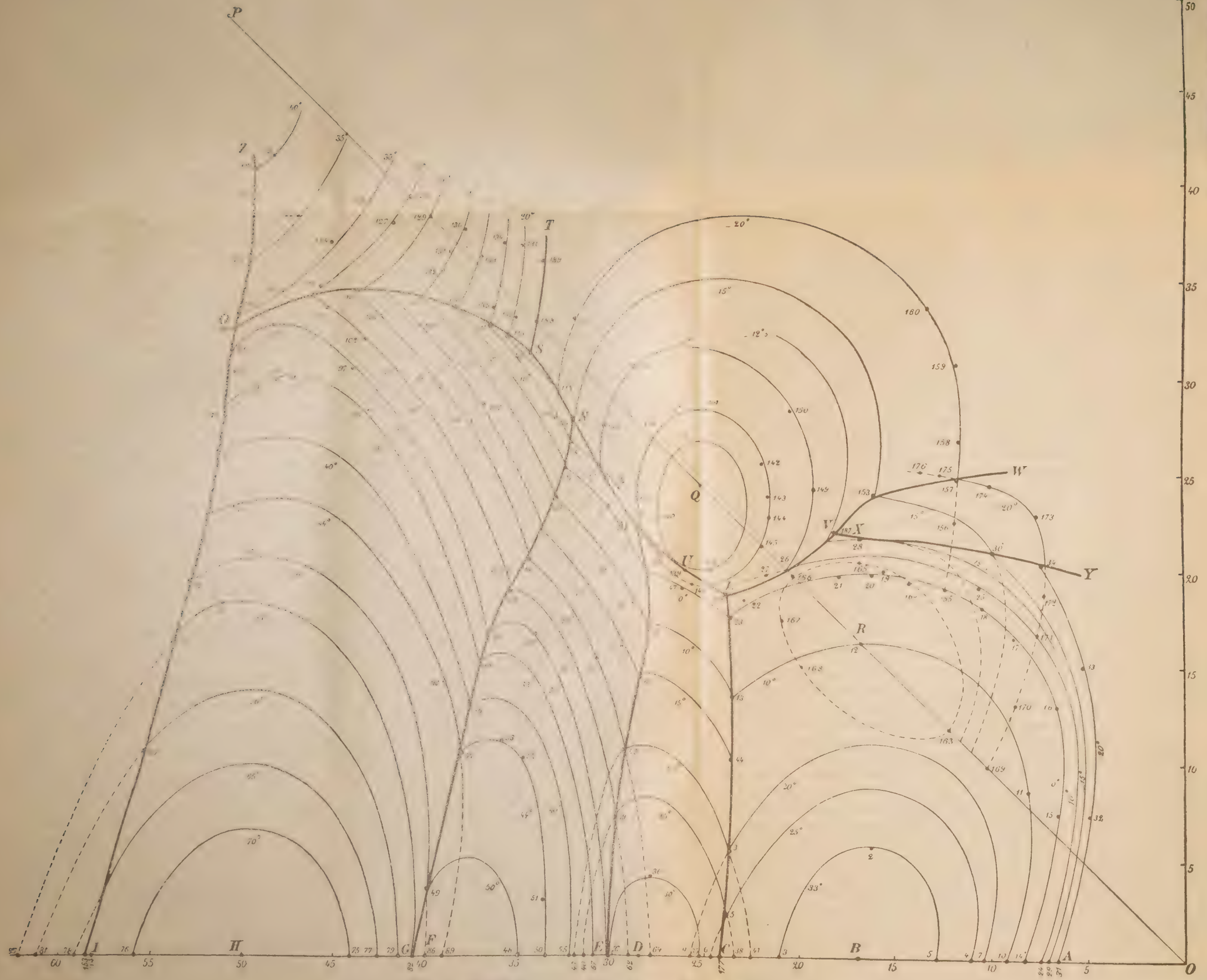

FIG. 134.—Isothermal curves for the system $FeCl_3$—HCl—H_2O.

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melts with separation of $2FeCl_3,12H_2O$, just as carnallite melts at 168° with separation of potassium chloride.

The Isothermal Curves.—A deeper insight into the behaviour of the system $FeCl_3$—HCl—H_2O is obtained from a study of the isothermal curves, the complete series of which, so far as they have been studied, is given in Fig. 134.[1] In this figure the lightly drawn curves represent isothermal solubility curves, the particular temperature being printed beside the curve.[2] The dark lines give the composition of the univariant systems at different temperatures. The point of intersection of a dark with a light curve gives the composition of the univariant solution at the temperature represented by the light curve; and the point of intersection of two dark lines gives the composition of the invariant solution in equilibrium with three solid phases. The dotted lines represent metastable systems, and the points P, Q, and R represent solutions of the composition of the ternary salts, $2FeCl_3,2HCl,4H_2O$; $2FeCl_3,2HCl,8H_2O$; and $2FeCl_3,2HCl,12H_2O$.

The farther end of the model (Fig. 133) corresponds, as already mentioned, to the temperature — 30°, so that the outline evidently represents the isothermal curve for that temperature. Fig. 134 does not show this. We can, however, follow the isothermal for — 20°, which is the extreme curve on the right in Fig. 134. Point A represents the solubility of $2FeCl_3,12H_2O$ in water. If hydrogen chloride is added, the concentration of ferric chloride in the solution first decreases and then increases, until at point 34 the ternary double salt $2FeCl_3,2HCl,12H_2O$ is formed. If the addition of hydrogen chloride is continued, the ferric chloride disappears ultimately, and only the ternary double salt remains. This salt can coexist with solutions of the composition represented by the curve which passes through the points 173, 174, 175. At the last-mentioned point, the ternary salt with $8H_2O$ is formed. The composition of the solutions with which this salt is in equilibrium at — 20° is represented by the curve which passes through a point of maximal concentration with respect to HCl, and cuts the curve SN at the point 112, at which the solution is in equilibrium with the two solid phases $2FeCl_3,4H_2O$, and $2FeCl_3,2HCl,8H_2O$. The succeeding portion of the isotherm represents the solubility curve at — 20° of $2FeCl_3,4H_2O$, which cuts the dark line OS at point 113, at which the solution is in equilibrium with the two solid phases $2FeCl_3,4H_2O$ and $2FeCl_3,2HCl,4H_2O$. Thereafter comes the solubility curve of the latter compound.

The other isothermal curves can be followed in a similar manner. If the temperature is raised, the region of existence of the ternary double salts becomes smaller and smaller, and at temperatures above 30° the ternary salts with $12H_2O$ and $8H_2O$ are no longer capable of

[1] These curves represent only portions of the isotherms, since the systems in which a ternary solution is in equilibrium with solid hydrogen chloride or a hydrate have not been investigated.

[2] The numbers printed beside the points on the curves refer to the number of the experiment in the original paper.

existing. If the temperature is raised above 46°, only the binary compounds of ferric chloride and water and the anhydrous salt can exist as solid phases. The isothermal curve for 0° represents the solubility curve for $2FeCl_3,12H_2O$; $2FeCl_3,7H_2O$; $2FeCl_3,5H_2O$; and $2FeCl_3,4H_2O$.

Finally, in the case of the system $FeCl_3$—HCl—H_2O, we find *closed* isothermal curves. Since, as already stated, the salt $2FeCl_3,2HCl,8H_2O$ has a definite melting-point, the temperature of which is therefore higher than that at which this compound is in equilibrium with solutions of other composition, it follows that the line of intersection of an isothermal plane corresponding with a temperature immediately below the melting-point of the salt with the cone-shaped surface of its region of existence will form a closed curve. This is shown by the isotherm for — 4·5°, which surrounds the point Q, the melting-point of the ternary salt.

The following table gives some of the numerical data from which the curves and the model have been constructed :—

Point.	Solid Phases.	Temperature.	Composition of the solution in gm.-mols. salt to 100 gm.-mols. water.	
			HCl.	$FeCl_3$.
A	$2FeCl_3,12H_2O$	— 20°	—	6·56
C	$2FeCl_3,12H_2O$; $2FeCl_3,7H_2O$	27·4°	—	24·30
E	$2FeCl_3,7H_2O$; $2FeCl_3,5H_2O$	30°	—	30·24
G	$2FeCl_3,5H_2O$; $2FeCl_3,4H_2O$	55°	—	40·64
J	$2FeCl_3,4H_2O$; $FeCl_3$	66°	—	58·40
L	$2FeCl_3,12H_2O$; $2FeCl_3,7H_2O$; $2FeCl_3,2HCl,8H_2O$	— 7·5°	19·22	23·72
M	$2FeCl_3,7H_2O$; $2FeCl_3,5H_2O$; $2FeCl_3,2HCl,8H_2O$	— 7·3°	23·08	28·55
N	$2FeCl_3,5H_2O$; $2FeCl_3,4H_2O$; $2FeCl_3,2HCl,8H_2O$	— 16°	28·40	31·89
S	$2FeCl_3,4H_2O$; $2FeCl_3,2HCl,8H_2O$; $2FeCl_3,2HCl,4H_2O$	— 27·5°	32·33	34·21
O	$2FeCl_3,4H_2O$; $FeCl_3$; $2FeCl_3,2HCl,4H_2O$	29°	33·71	49·84
U	$2FeCl_3,7H_2O$; $2FeCl_3,2HCl,8H_2O$	— 4·5°	20·66	25·74
V	$2FeCl_3,12H_2O$; $2FeCl_3,2HCl,12H_2O$; $2FeCl_3,2HCl,8H_2O$	— 13°	22·40	18·00
X	$2FeCl_3,12H_2O$; $2FeCl_3,2HCl,12H_2O$	— 12·5°	22·14	16·69
Q	$2FeCl_3,2HCl,8H_2O$	— 3° (melting-point)		

Basic Salts.—Another class of systems in the study of which the Phase Rule has performed exceptional service is that of the basic salts. In many cases it is impossible, by the ordinary methods of analysis, to

decide whether one is dealing with a definite chemical individual or with a mixture. The question whether a solid phase is a chemical individual can, however, be answered, in most cases, with the help of the principles which we have already learnt. Let us consider, for example, the formation of basic salts from bismuth nitrate, and water. In this case we can choose as components Bi_2O_3, N_2O_5, and H_2O; since all the systems consist of these in varying amounts. If we are dealing with a condition of equilibrium at constant temperature between liquid and solid phases, three cases can be distinguished,[1] viz. :—

1. The solutions in different experiments have the same composition, but the composition of the precipitate alters. In this case there must be two solid phases.
2. The solutions in different experiments can have varying composition, while the composition of the precipitate remains unchanged. In this case only one solid phase exists, a definite compound.
3. The composition both of the solution and of the precipitate varies. In this case the solid phase is a solid solution or a mixed crystal.

In order, therefore, to decide what is the nature of a precipitate produced by the hydrolysis of a normal salt, it is only necessary to ascertain whether and how the composition of the precipitate alters with alteration in the composition of the solution. If the composition of the solution is represented by abscissæ, and the composition of the precipitate by ordinates, the form of the curves obtained would enable us to answer our question; for vertical lines would indicate the presence of two solid phases (1st case), horizontal lines the presence of only one solid phase (2nd case), and slanting lines the presence of solid solutions (3rd case). This method of representation cannot, however, be carried out in most cases. It is, however, generally possible to find one pair or several pairs of components, the *relative amounts* of which in the solution or in the precipitate undergo change when, and only when, the composition of the solution or of the precipitate changes. Thus, in the case of bismuth nitrate and water, we can represent the ratio of $Bi_2O_3 : N_2O_5$

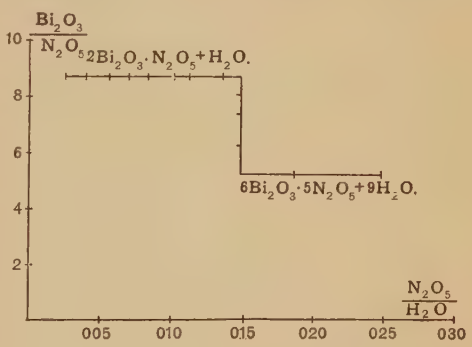

FIG. 135.

[1] Lash Miller and Kenrick, *J. Physical Chem.*, 1903, **7**, 259; Allan, *Amer. Chem. J.*, 1901, **25**, 307.

in the precipitate as ordinates, and $N_2O_5 : H_2O$ in the solution as abscissæ. A horizontal line then indicates a single solid phase, and a vertical line two solid phases. An example of this is given in Fig. 135.[1]

Bi_2O_3—N_2O_5—H_2O.—Although various systems have been studied in which there is formation of basic salts,[2] we shall content ourselves here with the description of some of the conditions for the formation of basic salts of bismuth nitrate, and for their equilibrium in contact with solutions.[3]

Three normal salts of bismuth oxide and nitric acid are known, *viz.* $Bi_2O_3,3N_2O_5,10H_2O(S_{10})$; $Bi_2O_3,3N_2O_5,4H_2O(S_4)$; and Bi_2O_3, $3N_2O_5,3H_2O(S_3)$. Besides these normal salts, there are the following basic salts :—

$Bi_2O_3,N_2O_5,2H_2O$	(represented by	B_{1-1-2})
Bi_2O_3,N_2O_5,H_2O	(,,	,, B_{1-1-1})
$6Bi_2O_3,5N_2O_5,9H_2O$	(,,	,, B_{6-5-9})
$2Bi_2O_3,N_2O_5,H_2O$	(,,	,, B_{2-1-1})

Probably some others also exist. The problem now is to find the conditions under which these different normal and basic salts can be in equilibrium with solutions of varying concentration of the three components. Having determined the equilibrium conditions for the different salts, it is then possible to construct a model similar to that for $MgCl_2$—KCl—H_2O or for $FeCl_3$—HCl—H_2O, from which it will be possible to determine the limits of stability of the different salts, and to predict what will occur when we bring the salts in contact with solutions of nitric acid of different concentrations and at different temperatures.

For our present purpose it is sufficient to pick out only some of the equilibria which have been studied, and which are represented in the model (Fig. 136). In this case use has been made of the triangular method of representation, so that the surface of the model lies within the prism.

This model shows the three surfaces, A, B, and C, which represent the conditions for the stable existence of the salts B_{1-1-1}, S_{10}, and S_3 in contact with solution at different temperatures. The front surface of the model represents the temperature 9°, and the farther end the temperature 75·5°. The dotted curve represents the isotherm for 20°. The prominences between the surfaces represent, of course, solutions which are saturated in respect of two solid phases. Thus, for example, *pabc* represents solutions in equilibrium with B_{1-1-1} and S_{10}; and the ridge *qde*, solutions in equilibrium with S_{10} and S_3. The point *b*, which lies at 75·5°, is the point of maximum temperature for S_{10}. If

[1] Allan, *Amer. Chem. J.*, 1901, **25**, 307.

[2] Hoitsema, *Z. physikal. Chem.*, 1895, **17**, 651; Allan, *loc. cit.*; Ruer, *Z. anorgan. Chem.*, 1906, **49**, 365.

[3] Rutten, *Z. anorgan. Chem.*, 1902, **30**, 342. Compare the system BeO—SO_3—H_2O; Parsons, *ibid.*, 1904, **42**, 250.

the temperature is raised above this point, S_{10} decomposes into the basic salt B_{1-1-1} and solution. This point is therefore analogous to the point M in the carnallite model, at which this salt decomposes into potassium chloride and solution (p. 250); or to the point at which the salt $2FeCl_3,2HCl,12H_2O$ decomposes into $2FeCl_3,12H_2O$ and solution (p. 257). The curve *pab* has been followed to the tempera-

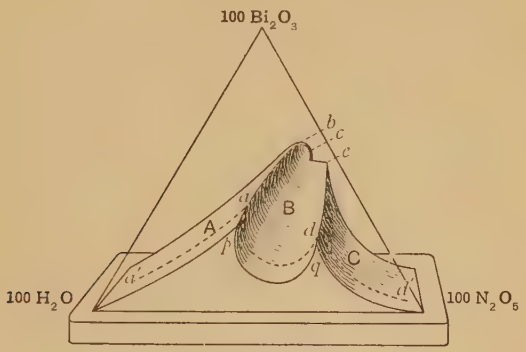

FIG. 136.

ture of 72° (point *c*). The end of the model is incomplete, but it is probable that in the neighbourhood of the point *c* there exists a quintuple point at which the basic salt B_{1-2-2} appears. In the neighbourhood of *e* also there probably exists another quintuple point at which S_4 is formed. These systems have, however, not been studied.

The following tables give some of the numerical data :—

ISOTHERM FOR 20°

Solid phase.	Composition of the solution. Gram-mols. in 1000 gram-mols. of water.	
	Bi_2O_3.	N_2O_5.
B_{1-1-1}	10·50	38·65
—	27·20	83·84
B_{1-1-1}; S_{10}	30·15	97·97
S_{10}	29·70	96·57
—	19·65	98·76
—	10·51	162·58
—	33·51	355·87
S_{10}; S_3	51·00	403·0
S_3	14·35	492·0
—	7·45	592·9

SYSTEMS IN EQUILIBRIUM WITH B_{1-1-1} AND S_{10} (CURVE *pabc*).

Temperature.	Composition of the solution. Gram-mols. in 1000 gram-mols. of water.	
	Bi_2O_5.	N_2O_5.
9°	26·7	88·2
20° (point *a*)	30·15	97·97
30°	33·6	112·3
50°	41·8	148·4
65°	57·21	190·8
75·5° (point *b*)	87·9	288·4
72° (point *c*)	96·0	327·0

SYSTEMS IN EQUILIBRIUM WITH S_{10} AND S_3 (CURVE *qde*).

Temperature.	Composition of the solution. Gram-mols. in 1000 gram-mols. of water.	
	Bi_2O_5.	N_2O_5.
11·5°	44·5	396
20°	51·0	405·4
50°	66·5	444·2
65°	80·0	454·4

Basic Mercury Salts.—The Phase Rule has also been applied by A. J. Cox [1] in an investigation of the basic salts of mercury, the result of which has been to show that, of the salts mentioned in text-books, quite a number are incorrectly stated to be chemical compounds or chemical individuals (p. 70). The investigation, which was carried out essentially in the manner described above, included the salts mentioned in the following table; and of the basic salts said to be derived from them, only those mentioned really exist. In the following table, the numbers in the second column give the minimum values of the concentration of the acid, expressed in equivalent normality, necessary for the existence of the corresponding salts in contact with solution at the temperature given in the third column.

Mercuric fluoride does not form any basic salt.

Since two succeeding members of a series can coexist only in contact with a solution of definite concentration, we can prepare acid solutions of definite concentration by bringing an excess of two such salts in contact with water.[2]

[1] *Z. anorgan Chem.*, 1904, **40**, 146.

[2] For a study of equilibria in the case of acid salts, see Koppel and Blumenthal, *Z. anorgan. Chem.*, 1907, **53**, 228.

Salt.	Normality of acid.	Temperature.
$HgCrO_4$	1·41	50°
$3HgO \cdot CrO_3$	$2·6 \times 10^{-4}$	50°
$Hg(NO_3)_2 \cdot H_2O$	18·72	25°
$3HgO \cdot N_2O_5$	0·159	25°
$HgSO_4$	6·87	25°
$3HgO \cdot SO_3$	$1·3 \times 10^{-3}$	25°
HgF_2	1·14	25°
$HgNO_3 \cdot H_2O$	2·95	25°
$5Hg_2O \cdot 3N_2O_5 \cdot 2H_2O$	ca. 0·293	25°
$2Hg_2O \cdot N_2O_5$(?)	0·110	25°
$3Hg_2O \cdot N_2O_5 \cdot 2H_2O$ (?)	$1·7 \times 10^{-3}$	25°
Hg_2SO_4	$4·2 \times 10^{-3}$	25°
$2Hg_2O \cdot SO_3 \cdot H_2O$	$5·6 \times 10^{-4}$	25°

Indirect Determination of the Composition of the Solid Phase.—It has already been shown (p. 111) how the composition of the solid phase in a system of two components can be determined without analysis, and we shall now describe how this can be done in a system of three components.[1]

We shall assume that we are dealing with the aqueous solution of two salts which can give rise to a double salt, in which case we can represent the solubility relations in a system of rectangular co-ordinates. In this case we should obtain, as before, the isotherm *adcb* (Fig. 137), if we express the composition of the solution in gram-molecules of A or of B to 100 gram-molecules of water.

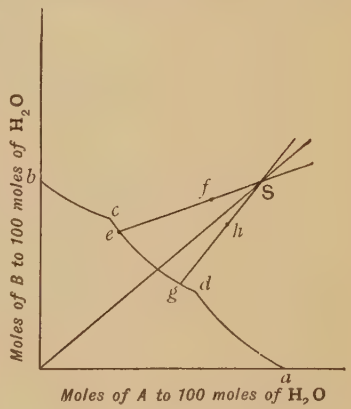

FIG. 137.

Let us suppose that the double salt is in equilibrium with the solution at a definite temperature, and that the composition of the solution is represented by the point *e*. The greater part of the solution is now separated from the solid phase, and the latter, *together with the adhering mother liquor*, is analysed. The composition (expressed, as before, in gram-molecules of A and B to 100 gram-molecules of water) will be represented by a point (*e.g. f*) on the line *e*S, where S represents the composition of the double salt.

[1] Schreinemakers, *Z. physikal. Chem.*, 1893, **11**, 76; Bancroft, *J. Physical Chem.*, 1902, **6**, 179.

That this is so will be evident when one considers that the composition of the whole mass must lie between the composition of the solution and that of the double salt, no matter what may be the relative amounts of the solid phase and the mother liquor.

If, in a similar manner, we analyse a solution of a different composition in equilibrium with the same double salt (not necessarily at the same temperature as before), and also the mixture of solid phase and solution, we shall obtain two other points, as, for example, *g* and *h*, and the line joining these must likewise pass through S. The method of finding the composition of an unknown double salt consists, therefore, in finding, in the manner just described, the position of two lines such as *ef* and *gh*. The point of intersection of these lines then gives the composition of the double salt.

If the double salt is anhydrous, the point S lies at infinity, and the lines *ef* and *gh* are parallel to each other.

The same result is arrived at by means of the triangular method of representation.[1]

It has already been pointed out (p. 239) that a point such as *x* (Fig. 116, p. 239), lying within the triangle A*ac*, represents mixtures of the solid phase A and a solution saturated with respect to A. If, therefore, the solid phase plus adhering saturated solution is analysed, and if the composition of the corresponding saturated solution is determined, then the line joining the composition of the saturated solution with the composition of the mixture (*e.g.* *x* in Fig. 116) will pass through the point representing the composition of the solid phase. Consequently, if the composition of different saturated solutions and of corresponding mixtures of solid phase plus saturated solution is determined, the lines joining the corresponding values of the composition will intersect at the point representing the composition of the solid phase. If the solid phase is a pure component (anhydrous), the lines will all pass through a corner of the triangle (*e.g.* Fig. 116); if the solid phase is an anhydrous double salt, the lines will intersect at a point on one side AB of the triangle (*e.g.* Fig. 117); if the solid phase is a hydrated component, the lines will intersect at a point on the side, A—H_2O or B—H_2O, of the triangle; and, lastly, if the solid phase is a hydrated double salt, the point of intersection will lie inside the triangle.

[1] *Z. anorgan. Chem.*, 1904, **40**, 148. See also Sahmen and von Vegesack, *Z. physikal. Chem.*, 1907, **59**, 257, 507; Jänecke, *ibid.*, 697.

CHAPTER XVI.

PRACTICAL APPLICATIONS OF EQUILIBRIUM DIAGRAMS.

HAVING discussed qualitatively the application of the Phase Rule to three-component systems formed by water and two salts with a common ion, one may now consider how the equilibrium diagrams, constructed on the basis of experimental data, can be employed in the quantitative study of the behaviour of such systems, and can be used to guide the practical operations of the winning of salts by crystallisation from solution.[1]

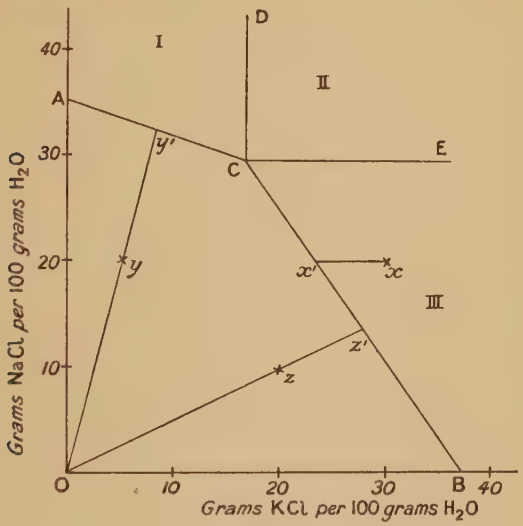

FIG. 138.

The System Sodium Chloride—Potassium Chloride—Water.—This may be taken as an illustration of a simple system in which there is no double-salt formation, and in which, at all temperatures above 0°, the salts crystallise anhydrous from solution.

[1] See Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344; Hildebrand, *ibid.*, 1918, **10**, 96; Reinders, *Z. anorgan. Chem.*, 1915, **93**, 202; Freeth, *Rec. trav. chim.*, 1924, **43**, 475; *Thesis*, Leiden, 1924; Hamid, *J. Soc. Chem. Ind.*, 1926, **45**, 315 T; Schloesing, *Compt. rend.*, 1920, **171**, 977.

On determining the composition of the solutions in equilibrium with each of the single salts alone and with a mixture of the two salts (see p. 240), the following values are obtained:—[1]

Temperature.	Solid phase.	Composition of solution.			
		In grams of salt per 100 grams of water.		In grams of salt per 100 grams of solution.	
		NaCl.	KCl.	NaCl.	KCl.
0°	NaCl	34·95	—	25·90	—
	KCl	—	28·20	—	22·0
	NaCl + KCl	31·53	10·55	22·19	7·43
25°	NaCl	35·63	—	26·28	—
	KCl	—	36·96	—	26·98
	NaCl + KCl	29·88	16·28	20·44	11·14
50°	NaCl	36·50	—	26·74	—
	KCl	—	43·12	—	30·14
	NaCl + KCl	29·09	22·03	19·25	14·58
75°	NaCl	37·75	—	27·39	—
	KCl	—	49·70	—	33·20
	NaCl + KCl	27·87	29·06	17·76	18·52
100°	NaCl	39·40	—	28·27	—
	KCl	—	56·20	—	35·97
	NaCl + KCl	27·39	35·16	16·85	21·62

The above values may be plotted either in rectangular co-ordinates (p. 240) or in a triangular diagram (p. 238).[2] When the numbers are plotted in rectangular co-ordinates, curves such as AC, BC (Fig. 138),[3] are obtained. Curve AC gives the composition of solutions, expressed in grams of anhydrous salt per 100 grams of water, in equilibrium with sodium chloride as solid phase; and the curve BC, similarly, represents solutions in equilibrium with potassium chloride. Point C gives the composition of the solution in equilibrium with both salts as solid phases.

As we have already learned (p. 241), a point in area I. represents the total composition of a mixture which is composed of solid sodium chloride and saturated solution represented by a point on the curve AC; a point in area II., a mixture of the two solid salts plus solution of composition C; and a point in area III., a mixture of solid potassium chloride and saturated solution represented by a point on the

[1] See Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

[2] It is important that the student should himself prepare the graphs referred to in this chapter, using a moderately large scale.

[3] Fig. 138 represents the isothermal for 25°.

curve BC. Mixtures having a composition represented by a point in the area ACBO are unsaturated solutions.

The equilibrium (solubility) diagram, having been plotted to scale, may now be used for the purpose of giving information regarding the quantitative behaviour of mixtures of sodium chloride, potassium chloride and water of any given composition, at the temperature of the isothermal. Thus: What will be the result of shaking together at 25°, 20 grams of sodium chloride, 30 grams of potassium chloride, and 100 grams of water? From the solubility diagram it is found that a mixture of this composition is represented by a point x (Fig. 138) lying in the area III. The mixture, therefore, must yield a saturated solution represented by a point on the curve BC, together with solid potassium chloride. To find the composition of the saturated solution, a line xx' is drawn parallel with the horizontal axis, and the point x', where this line cuts the solubility curve, gives the composition of the saturated solution. From the curve, x' is found to represent a solution composed of 20 grams of sodium chloride and 23·1 grams of potassium chloride per 100 grams of water. The original mixture, therefore, gives 6·9 grams of solid potassium chloride and 143·1 grams of saturated solution of the composition just given.

A mixture of the composition, 20 grams of sodium chloride, 5 grams of potassium chloride, and 100 grams of water, is represented by the point y (Fig. 138). At 25°, therefore, this mixture forms an unsaturated solution. On evaporating this solution at 25°,[1] the composition will change as shown by the line yy' (see p. 244), and when the composition reaches the point y' further evaporation will lead to the deposition of solid sodium chloride. The composition of the solution will then change in the direction y'C, and at C, solid potassium chloride will also begin to separate out.

How much water must be evaporated off before sodium chloride begins to be deposited, and how much pure sodium chloride can be obtained by isothermal evaporation of the solution at 25°?

From the solubility curve it is found that y' has the composition, 32·8 grams of sodium chloride and 8·2 grams of potassium chloride per 100 grams of water. Since, in the original solution, the ratio of sodium chloride to water was 20 : 100, and, in the solution y', the ratio is 32·8 : 100, an amount of water x must have been lost by the original 125 grams of solution sufficient to bring the ratio of salt to water up to the value 32·8 : 100. That is, $20 : (100 - x) = 32{\cdot}8 : 100$. From this, $x = 39{\cdot}0$ grams. When evaporation has been carried out to the point y', therefore, the original 125 grains of solution will have diminished to 86 grams, consisting of 20 grams of sodium chloride, 5 grams of potassium chloride, and 61 grams of water.

Further evaporation leads to the point C, which has the composition, 29·88 grams of sodium chloride and 16·28 grams of potassium

[1] If the evaporation is carried out at some other temperature, say 100°, the corresponding isothermal solubility curve must be constructed.

chloride to 100 grams of water. Since, at the point y', the solution contains only 8·2 grams of potassium chloride to 100 grams of water, 141 grams of solution of composition y' must lose x' grams of water to give a solution of the composition C. To obtain the value of x', we have $8{\cdot}2 : (100 - x') = 16{\cdot}28 : 100$. Hence, $x' = 49{\cdot}6$ grams. The amount of water lost by 86 grams of solution y' would therefore be 30·3 grams.

The amount of sodium chloride deposited during evaporation of the solution from the point y' to the point C can be obtained as follows. For a constant amount of water, the ratio of sodium chloride to potassium chloride diminishes from 32·8/8·2 at y' to 29·88/16·28 at C. The amount of sodium chloride, w, therefore, which must separate out is given by the expression $32{\cdot}8 - w : 8{\cdot}2 = 29{\cdot}88 : 16{\cdot}28$, from which one calculates $w = 17{\cdot}75$. This is the weight of sodium chloride in grams which will separate when 141 grams of solution y' is evaporated at 25° until the point C is reached. From 86 grams of solution y', therefore, composed of 20 grams of sodium chloride, 5 grams of potassium chloride and 61 grams of water, 10·83 grams of sodium chloride would be deposited; and since, as we have seen, 30·3 grams of water would also evaporate away, the original 125 grams of unsaturated solution, when evaporated at 25° until the point C is reached, will have diminished to 44·97 grams of solution consisting of $(20 - 10{\cdot}83) = 9{\cdot}27$ grams of sodium chloride, 5 grams of potassium chloride, and $(100 - 39 - 30{\cdot}3) = 30{\cdot}7$ grams of water.

In the same way, one can calculate the amount of water which will have to be evaporated off and the weight of potassium chloride which will be deposited when the unsaturated solution z, consisting of 20 grams of potassium chloride, 10 grams of sodium chloride, and 100 grams of water is evaporated at 25°, until the point C is reached.

Separation of Salts by a Temperature-cycle Process.—For the practical separation of two salts with a common ion, advantage may be taken, when possible, of the variation of the solubility of salts with the temperature, and by alternate evaporation at a higher temperature and cooling to a lower temperature, an efficient separation of the salts may be effected. Such a cyclical process can be illustrated by means of the system sodium chloride—potassium chloride—water.[1]

In Fig. 139, the curves ac, cb, represent the isothermal for 0°, and the curves $a'c'$, $c'b'$, the isothermal for 100°. If the original unsaturated solution, x, representing a mixture of 20 grams of sodium chloride, 14 grams of potassium chloride, and 100 grams of water is evaporated at a temperature of 100°, the composition of the solution alters along the line xx'. On continued evaporation, the solution then changes in the direction c'. At this point the sodium chloride which has been deposited is separated from the solution, which is then cooled down to 0°. During this process the composition of the mixture alters in the direction $c'y$. Since this curve lies in the area for potassium chloride and

[1] Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

represents solutions which are supersaturated for potassium chloride, this salt will be deposited, until, at 0°, the solution attains the composition represented by y. At this point the solid potassium chloride is separated from the solution. If the solution y is now evaporated at 100°, deposition of sodium chloride takes place at the composition y', and the deposition continues until the point c' is again reached. The salt is separated and the solution cooled as before. This cycle of operations, which yields first sodium chloride and then potassium

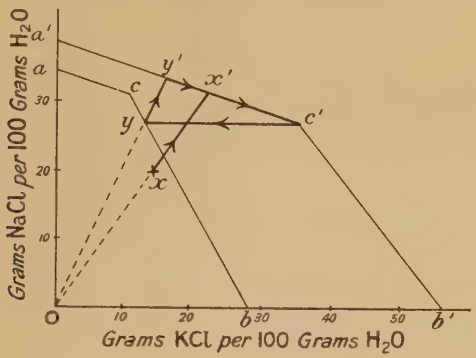

FIG. 139.

chloride, can be continued until all the solution is used up, or fresh solution can be introduced into the system at each evaporation. From what has already been said in the preceding section, it will be easy to calculate, from the solubility data and the solubility diagram, the amount of water which must be evaporated off at each cycle and the amount of solid salt which will be deposited, and so the process can be controlled. The following numbers, given by Blasdale, will serve as illustration :—

	Composition of the solution.			Substances eliminated.
	NaCl.	KCl.	H_2O.	
At the outset .	20	14	100	—
At the point x' .	20	14	62·78	37·22 grams H_2O
,, ,, c' .	10·91	14	39·72	9·09 ,, NaCl 23·1 ,, H_2O
,, ,, y .	10·91	5·14	39·72	8·86 grams KCl
,, ,, y' .	10·91	5·14	31·83	7·89 ,, H_2O

Although the above cycle of operations has been carried out between the temperatures of 0° and 100°, it may also be carried out between any other two temperatures, *e.g.* 15° or 25° and 100°.[1] By

[1] See Turrentine and Tanner, *J. Ind. Eng. Chem.*, 1924, **16**, 242.

means of quantitative calculations carried out in the manner already discussed, the conditions under which the cycle of operations may be most economically conducted may readily be decided in any given case.

Potassium Chloride—Potassium Sulphate—Water.—The ease with which separation of mixtures of potassium chloride and sodium chloride into the pure salts can be effected is due to the fact that the solubility of potassium chloride varies considerably, whereas the solubility of sodium chloride varies but little with the temperature. That is, the ratio of KCl : NaCl in the solution saturated for the two salts (points c and c' in Fig. 138) varies markedly with the temperature. Such conditions, however, do not exist in the case of, say, potassium sulphate and potassium chloride.

The solubilities of these two salts at 0° and 100° are as follows :—

Temperature.	Solid phase.	Composition of solution in grams of salt per 100 grams of water.	
		KCl.	K_2SO_4.
0°	KCl	28·20	—
	K_2SO_4	—	7·23
	KCl + K_2SO_4	27·88	1·21
100°	KCl	56·20	—
	K_2SO_4	—	23·44
	KCl + K_2SO_4	54·43	2·83

On plotting these numbers, the diagram shown in Fig. 140 is obtained, the curve acb being the isothermal for 0°, and the curve $a'c'b'$ the isothermal for 100°.

When a solution of the composition x is evaporated at 100°, potas-

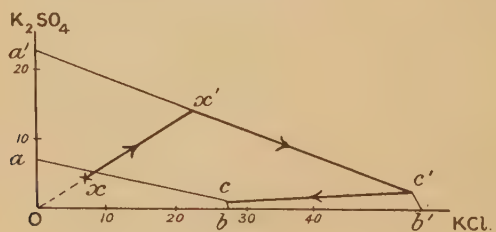

FIG. 140.

sium sulphate separates out at x', and continues to be deposited until the solution reaches the composition c'. At this point, the potassium sulphate may be separated from the solution. Solution c', as will be seen, lies in what corresponds with area II. in Fig. 138 (p. 265), and, consequently, when the solution is cooled down, separation of both potassium chloride and potassium sulphate takes place, until the

solution attains the composition c. Since the line joining O and c, when produced, cuts the curve $b'c'$, it follows that on evaporating the solution c at 100° potassium chloride will be deposited. The point of intersection, however, lies very near to the point c', so that only a small amount of potassium chloride, too small for industrial success, is deposited before the point c' is reached. In such a case as this, therefore, separation of the pure salts is not feasible, and one would have to be content with a separation into the potassium sulphate deposited in the first stage of the process and a mixture of the two salts containing about 5 per cent. of potassium sulphate.

In general, it can be said that when the ratio of the two salts in solutions saturated with respect to both salts at any two temperatures, t_1 and t_2, is the same, then separation of the two salts is impossible; and even when the ratio is not the same separation will be economically successful only when there is a sufficiently large variation of the ratio with temperature. In the case of potassium sulphate and potassium chloride, we find that the ratio $KCl : K_2SO_4$ is 23·04 at 0°, and 24·2 at 100°. The difference is too slight to make the separation feasible from an industrial point of view.

Ammonium Perchlorate—Ammonium Sulphate—Water.—An interesting example of a multiple cycle process has been worked out by Freeth [1] for the separation of a mixture of equal weights of ammonium perchlorate and ammonium sulphate. The solubility data on which the process was based are as follows:—

Temperature.	Solid phase.	Composition of solution per cent.		
		NH_4ClO_4.	$(NH_4)_2SO_4$.	H_2O.
25°	NH_4ClO_4	20·02	—	79·98
	$NH_4ClO_4 + (NH_4)_2SO_4$	3·0	41·70	55·30
	$(NH_4)_2SO_4$	—	43·5	56·5
60°	NH_4ClO_4	33·6	—	66·4
	$NH_4ClO_4 + (NH_4)_2SO_4$	8·2	40·9	50·9
	$(NH_4)_2SO_4$	—	46·8	53·2

For the process of separation, the following flow-sheet was constructed. From 9823 grams of a mixture, having the composition 39·6 per cent. $(NH_4)_2SO_4$, 7·9 per cent. NH_4ClO_4 and 52·5 per cent. H_2O, there were deposited at 25°, 500 grams of perchlorate, and a mother liquor (9323 grams) was left having the composition 41·7 per cent. $(NH_4)_2SO_4$, 3·0 per cent. NH_4ClO_4, and 55·3 per cent. H_2O. This solution was evaporated at 60° until 318 grams of water had passed off, the concentrated solution (9005 grams) having the composition, 43·2 per cent. $(NH_4)_2SO_4$, 3·1 per cent. NH_4ClO_4, and 53·7 per cent. H_2O. To this solution, at 60°, there was added a mixture of 500 grams

[1] *Thesis*, Leiden, 1924.

of $(NH_4)_2SO_4$ and 500 grams of NH_4ClO_4, giving 10,005 grams of a mixture of the composition 43·9 per cent. $(NH_4)_2SO_4$, 7·8 per cent. NH_4ClO_4, and 48·3 per cent. H_2O. From this mixture 500 grams of ammonium sulphate separated at 60°, yielding a mother liquor (9505 grams) of the composition 40·9 per cent. $(NH_4)_2SO_4$, 8·2 per cent. NH_4ClO_4, and 50·9 per cent. H_2O. To this solution 318 grams of water were added, and the temperature lowered to 25°. This completes the cycle, the mixture now being the same as the original one. This cyclical process could be repeated time after time, and at each cycle there is obtained, from the quantities taken, 500 grams of pure ammonium perchlorate and 500 grams of pure ammonium sulphate.[1]

By means of similar cyclical processes, a separation can be effected in the case of the salts potassium sulphate and potassium nitrate, potassium nitrate and sodium nitrate, sodium sulphate and sodium nitrate.[2]

When the two salts give rise to a double salt, a more complicated procedure may be necessary for the separation of the single salts. A good example of this is given by the system ammonium sulphate—sodium sulphate—water, studied by Matignon and Meyer,[3] Dawson,[4] and Freeth.[5]

Ammonium Sulphate—Sodium Sulphate—Water.—This system differs markedly from those discussed in the preceding pages in the fact that a double salt, $(NH_4)_2SO_4$, Na_2SO_4, $4H_2O$, is formed, which decomposes into the single salts at 59·3°. One of the component salts, also, crystallises from solution in the hydrated form, namely, Na_2SO_4, $10H_2O$, at temperatures below 32°. At 60° only the anhydrous single salts are stable.

The solubility values at 25° and at 60° are given in the following tables :—[6]

Temperature.	Solid phase.	Composition of solution per cent.		
		$(NH_4)_2SO_4$.	Na_2SO_4.	H_2O.
25°	$(NH_4)_2SO_4$	43·4	—	56·6
	$(NH_4)_2SO_4 + (NH_4)_2SO_4$, Na_2SO_4, $4H_2O$	38·7	8·2	53·1
	$(NH_4)_2SO_4$, Na_2SO_4, $4H_2O$ + Na_2SO_4, $10H_2O$	14·10	25·76	60·14
	Na_2SO_4, $10H_2O$	—	21·71	78·29
60°	$(NH_4)_2SO_4$	46·80	—	53·20
	$(NH_4)_2SO_4 + Na_2SO_4$	36·91	16·33	46·76
	Na_2SO_4	—	31·20	68·80

[1] The student should prepare a graph showing the course of the separation.

[2] Hamid, *J. Chem. Soc.*, 1926, pp. 199, 206 ; *J. Soc. Chem. Ind.*, 1926, **45**, 315 T. For other cases, see Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

[3] *Compt. rend.*, 1917, **165**, 787 ; 1918, **166**, 115, 686 ; *Annales Chim. Phys.*, 1918, **9**, 251.

[4] *J. Chem. Soc.*, 1918, **113**, 675.

[5] *Thesis*, Leiden, 1924.

[6] Freeth, *Thesis*, Leiden, 1924.

These values are represented graphically in Fig. 141, the triangular diagram being employed in this case. In this diagram the isothermal for 25° is represented by the curves AB, BC, CD, and the isothermal for 60° by the curves GH, HK. The lightly drawn lines delimit the areas of heterogeneous mixtures, as explained on page 239. Point E represents the composition of the hydrated double salt, and F the composition of sodium sulphate decahydrate.

Before passing to the description of the process by which a mixture of ammonium sulphate and sodium sulphate can be separated into

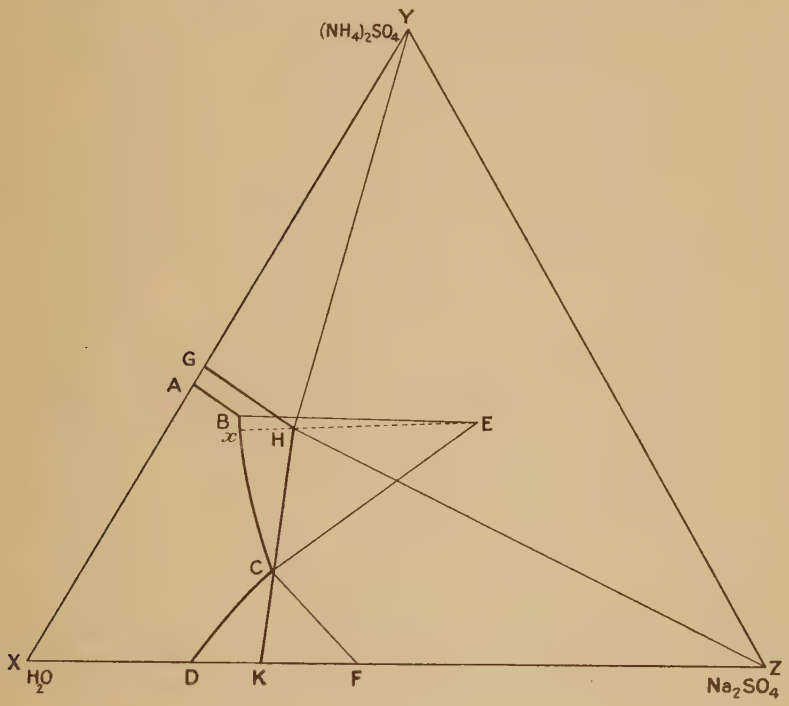

FIG. 141.

the single salts, attention may be drawn to the fact that point H, which represents the composition of a solution saturated for both sodium sulphate and ammonium sulphate at 60°, falls within the area for heterogeneous mixtures of double salt and solution at 25°. A mixture, therefore, which has the composition H will, at 25°, separate into solid double salt and a saturated solution, the composition of which will be given by joining EH and producing the line to meet the curve BC at x. Moreover, the relative weights of saturated solution and of solid double salt are given by the lengths of the lines EH and Hx.

The triangle GHY is the area of heterogeneous mixtures of solid

ammonium sulphate and saturated solution at 60°, and the triangle KHZ, similarly, is the area of heterogeneous mixtures of anhydrous sodium sulphate and saturated solutions at 60°.

Based on the solubility data given above, the following process for the separation of a mixture of equal amounts of sodium sulphate and ammonium sulphate has been worked out by Freeth, the cycle of operations being indicated in Fig. 142, which represents portions of the two isotherms in the neighbourhood of the points B and H in Fig. 141.

Starting at 60° with 2632 grams of a liquor of composition represented by the point E in Fig. 142, namely, 24·5 per cent. $(NH_4)_2SO_4$, 10·8 per cent. Na_2SO_4, and 64·7 per cent. H_2O, 917 grams of the double salt are added (which give a mixture of composition F), and then 1000 grams of a fifty-fifty mixture of the two salts. In this way 4549 grams of a mixture (point D) having the composition, 32·8 per cent. $(NH_4)_2SO_4$, 25·5 per cent. Na_2SO_4, and 41·7 per cent. H_2O are obtained. Since D corresponds to a point on the line HZ in Fig. 141, the mixture deposits anhydrous sodium sulphate (500 grams) and gives 4049 grams of solution of composition B (Fig. 142). This solution, which corresponds to point H in Fig. 141, and has the composition 36·9 per cent. $(NH_4)_2SO_4$, 16·3 per cent. Na_2SO_4, and 46·8 per cent. H_2O, is cooled to 25°, and is allowed to deposit 917 grams of the double salt, the amount required for adding to the diluted liquor at E (see above). The mother liquor, C (3132 grams), is concentrated at 60° until it has the composition represented by point A,[1] namely, 51·0 per cent. $(NH_4)_2SO_4$, 12·6 per cent. Na_2SO_4, and 36·4 per cent. H_2O, the amount of water evaporated off being 887 grams. Point A corresponds to a point on the line HY in Fig. 141, and so deposits solid ammonium sulphate (500 grams) and gives 1745 grams of solution B, the composition of which has already been given. The solution B is then diluted by the addition of 887 grams of water to give 2632 grams of unsaturated solution of composition E. The cycle has thus been completed, and in its course the 1000 grams of mixture have been separated into 500 grams of each of the single salts.

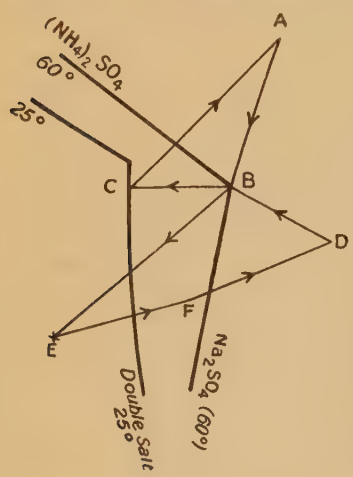

FIG. 142.

[1] The direction of the line CA is, of course, obtained by joining the angle of the triangle representing pure water (Fig. 141) with the point C and producing to A.

CHAPTER XVII.

SYSTEMS OF FOUR COMPONENTS.

In the systems which have so far been studied, we have met with cases where two or three components could enter into combination; but in no case did we find double decomposition occurring. The reason of this is that in the systems previously studied, in which double decomposition might have been possible, namely, in those systems in which two salts acted as components, the restriction was imposed that either the basic or the acid constituent of these salts must be the same; a restriction imposed, indeed, for the very purpose of excluding double decomposition. A system formed of water and three salts with a common ion will constitute a four-component system; and if the restriction that the salts have a common ion be allowed to drop, two salts along with water will give rise to a four-component system. In this case, double decomposition between the salts is possible.

Hitherto, in connection with four-component systems, the attention has been directed chiefly to the study of aqueous solutions of salts, and more especially of the salts which occur in sea-water, *i.e.* chiefly the sulphates and chlorides of magnesium, potassium, and sodium.[1] The importance of these investigations will be recognised when one recollects that by the evaporation of sea-water there have been formed the enormous salt-beds at Stassfurt, which constitute at present the chief source of the sulphates and chlorides of magnesium and potassium. The investigations, therefore, are not only of great geological interest as tending to elucidate the conditions under which these salt-beds have have been formed, but are of no less importance for the industrial working of the deposits.

Water and Three Salts with Common Ion.—Water and three salts with a common ion constitute a system of four components, and a brief discussion of such systems may be given here for the purpose more especially of explaining the methods by which the composition of such systems can be represented graphically.

Just as we saw (p. 238) that the equilateral triangle can be employed for the isothermal representation of the compositon of a ternary system, so, for the representation of the composition of a quaternary system one may employ a regular tetrahedron, each face of which is an equilateral triangle and the edges of which are all equal (Fig. 143). If the

[1] See, however, the researches of Schreinemakers, *Z. physikal. Chem.*, 1907 **59**, 641; 1910, **71**, 109.

four components, A, B, C, D, are represented by the four corners of the tetrahedron, then it is clear that points on one of the edges will represent binary systems, points on a triangular face will represent ternary systems, and points within the tetrahedron will represent quaternary systems. Thus, the point *a* (Fig. 143) represents the composition of a solution of the two components A and D in equilibrium with one solid phase (A); *d* represents the composition of the ternary solution, containing A, B, and D, in equilibrium with two solid phases (A and B); and *g* represents the composition of a quaternary solution in equilibrium with three solid phases A, B, and C. The composition represented by *g* can be obtained by drawing from *g* a line, parallel to AC or AB, so as to cut the face of the tetrahedron BCD. The length of this line gives the proportional (percentage) amount of A in the quaternary solution *g*. Similarly, by drawing lines parallel to AB or BC, and to AC or BC, so as to cut the faces ADC and ADB respectively, the length of the lines so obtained gives the proportional amounts of B and C. Lastly, by drawing from *g* a line parallel to AD, BD, or CD, so as to cut the face ABC, the amount of D in the quaternary mixture is obtained.

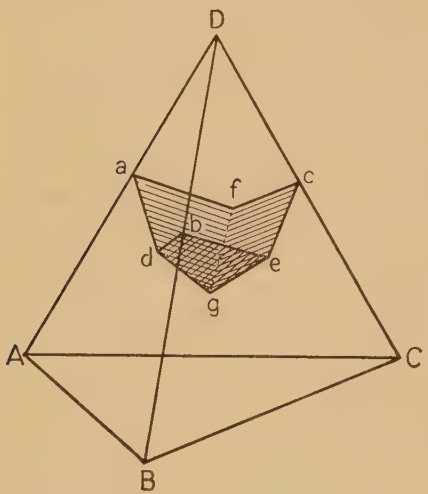

Fig. 143.

In Fig. 143, it may be mentioned, the curves *dg*, *eg*, and *fg* represent quaternary solutions in equilibrium with two solid phases, while the areas *adgf*, *bdge*, and *cegf* represent quaternary solutions in equilibrium with a single solid phase A, B, or C.

Although a three-dimensional method of representation is necessary in order to give a complete picture of the isothermal conditions in a quaternary system, it is very convenient, for practical purposes, to make use of a plane diagram. Such a diagram can be obtained by projecting the curves in Fig. 143 *perpendicularly* on the base of the tetrahedron.[1] The vertex of the tetrahedron (D) then comes to lie at the centre D of the triangle ABC (Fig. 144), and the edges AD, BD, and CD find their projections in the three medians AD, BD, and CD.

In order to plot the results of experiment in the plane triangular diagram, it has to be borne in mind that while the composition of the

[1] According to the method of Jänecke (p. 222), the curves are projected *perspectively*.

quaternary solution is expressed in terms of the four components, namely, x per cent. A, y per cent. B, z per cent. C, w per cent. D, the projection of this point in the tetrahedron can represent only the relative proportions, x', y', and z' of the three components A, B, and C. To obtain the position of this point in the triangular diagram, therefore, $\frac{w}{3}$ is added to the actual percentages x, y, and z, and we fix a point in the triangle such that $x' = x + \frac{w}{3}$, $y' = y + \frac{w}{3}$, and $z' = z + \frac{w}{3}$.

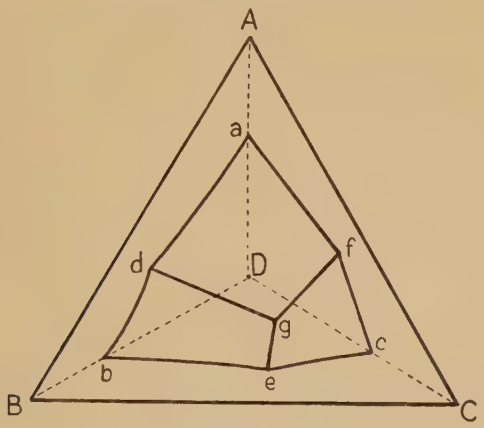

FIG. 144.

Lithium Sulphate, Ammonium Sulphate, Ferrous Sulphate, Water.—The equilibria in quaternary systems in which three salts with a common ion together with water are the components have been

PERCENTAGE COMPOSITION OF SOLUTIONS AT 30°.

Point.	Solid phase.	Per cent. $FeSO_4$.	Per cent. Li_2SO_4.	Per cent. $(NH_4)_2SO_4$.
a	$FeSO_4 . 7H_2O$	24·87	—	—
b	$Li_2SO_4 . H_2O$	—	25·1	—
c	$(NH_4)_2SO_4$	—	—	44·27
d	$FeSO_4 . 7H_2O + Li_2SO_4 . H_2O$	16·1	16·5	—
e	$Li_2SO_4 . H_2O + D_{Li}$	—	21·88	12·46
f	$(NH_4)_2SO_4 + D_{Li}$	—	6·59	39·55
g	$(NH_4)_2SO_4 + D_{Fe}$	0·79	—	43·86
h	$FeSO_4 . 7H_2O + D_{Fe}$	25·22	—	5·93
k	$FeSO_4 . 7H_2O + Li_2SO_4 . H_2O + D_{Fe}$	16·85	15·62	4·82
l	$Li_2SO_4 . H_2O + D_{Fe} + D_{Li}$	4·15	20·03	12·32
m	$(NH_4)_2SO_4 + D_{Fe} + D_{Li}$	0·61	6·23	40·48
p	D_{Fe}	13·13	—	11·45
q	D_{Li}	—	16·58	19·29

investigated by Schreinemakers,[1] and the results obtained in the case of the system water—lithium sulphate—ammonium sulphate—ferrous sulphate at 30° are represented in Fig. 145, and summarised in the table on p. 277.

The solid phases which occur are $(NH_4)_2SO_4 . Li_2SO_4 . H_2O$; $FeSO_4 . 7H_2O$; $Li_2SO_4 . (NH_4)_2SO_4$ (= D_{Li}); and $FeSO_4 . (NH_4)_2SO_4 . 6H_2O$ (= D_{Fe}). Since the double salt D_{Li} is anhydrous, it is represented by a point on the side of the triangle Li—NH_4; but the hydrated salts are represented by points within the triangle, as indicated in Fig. 145.

The different areas, *adkh*, *bdke*, etc., of the projection figure represent the composition of solutions with which the single solid phases $FeSO_4 . 7H_2O$, $Li_2SO_4 . H_2O$, etc., can exist. Since the curves separating two areas represent solutions in equilibrium with the two solid

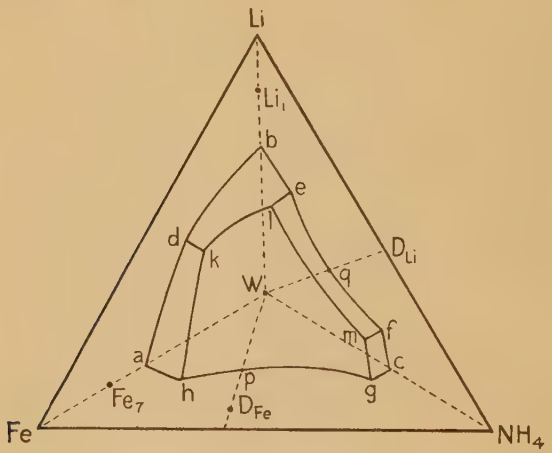

FIG. 145.

phases belonging to these areas, it follows that solid phases belonging to adjacent areas can coexist with solution, but solid phases belonging to areas which are not adjacent cannot coexist with solution. Thus $FeSO_4 . 7H_2O$ can coexist with $Li_2SO_4 . H_2O$ and with D_{Fe}, but it cannot coexist with D_{Li} nor with $(NH_4)_2SO_4$. From the figure we see that D_{Fe} can coexist with all the other solid phases in contact with solution.

RECIPROCAL SALT PAIRS.

Choice of Components.—When two salts undergo double decomposition, the interaction can be expressed by an equation such as

$$NH_4Cl + NaNO_3 = NaCl + NH_4NO_3$$

[1] *Z. physikal. Chem.*, 1908, **65**, 586; 1910, **71**, 109.

Since one pair of salts—$NaCl + NH_4NO_3$—is formed from the other pair—$NH_4Cl + NaNO_3$—by double decomposition, the two pairs of salts are known as *reciprocal salt-pairs*.[1] It is with systems in which the component salts form reciprocal salt-pairs that we have now to deal.

It must be noted that the four salts formed by two reciprocal salt-pairs do not constitute a system of four, but only of *three* components. This will be understood if it is recalled that only so many constituents are taken as components as are necessary to *express* the composition of all the phases present (p. 8); and it will be seen that the composition of each of the four salts which can be present together can be expressed in terms of three of them. Thus, for example, in the case of NH_4Cl, $NaNO_3$, NH_4NO_3, $NaCl$, we can express the composition of NH_4Cl by $NH_4NO_3 + NaCl - NaNO_3$; or of $NaNO_3$ by $NH_4NO_3 + NaCl - NH_4Cl$. In all these cases it will be seen that negative quantities of one of the components must be employed; but that we have seen to be quite permissible (p. 9). The *number* of components is, therefore, three; and any three of the four salts can be chosen.

Since, then, two reciprocal salt-pairs constitute only three components or independently variable constituents, another component is necessary in order to obtain a four-component system. As such, we shall choose water.

Transition Point.—In the case of the formation of double salts from two single salts, we saw that there was a point—the *quintuple point*—at which five phases could coexist. This point we also saw to be a transition point, on one side of which the double salt, on the other side the two single salts in contact with solution, were found to be the stable system. A similar behaviour is found in the case of reciprocal sal -pairs. The four-component system, two reciprocal salt-pairs and water, can give rise to an invariant system in which the six phases, four salts, solution, vapour, can coexist; the temperature at which this is possible constitutes a *sextuple point*. This sextuple point is also a transition point, on the one side of which the one salt-pair, on the other side the reciprocal salt-pair, is stable in contact with solution.

The sextuple point is the point of intersection of the curves of six univariant systems, viz. four solubility curves with three solid phases each, a vapour-pressure curve for the system: two reciprocal salt-pairs —vapour; and a transition curve for the condensed system: two reciprocal salt-pairs—solution. If we omit the vapour phase and work under atmospheric pressure (in open vessels), we find that the transition point is the point of intersection of four solubility curves.

[1] See especially Meyerhoffer, *Sitzungsber. Wien. Akad*, 1895, **104**, II. *b*, 840; Meyerhoffer and Saunders, *Z. physikal. Chem.*, 1899, **28**, 453; **31**, 370; Uyeda, *Mem. Coll. Sci. Eng. Kyoto*, 1902, **2**, 245. The investigation of the equilibria between reciprocal salt-pairs alone (three-component systems) is of great importance for the artificial preparation of minerals, as also in analytical chemistry for the proper understanding of the methods of conversion of insoluble systems into soluble by fusion (see Meyerhoffer, *Z. physikal. Chem.*, 1901, **38**, 307; Jänecke, *ibid.*, 1908, **64**, 305, 343; 1912, **80**, 1; 1913, **82**, 1).

Just as in the case of three-component systems we saw that the presence of one of the single salts along with the double salt was necessary in order to give a univariant system, so in the four-component systems the presence of a third salt is necessary as solid phase along with one of the salt-pairs. In the case of the reciprocal salt-pairs mentioned above, the transition point would be the point of intersection of the solubility curves of the systems with the following groups of salts as solid phases. Below the transition point :

$$NH_4Cl + NaNO_3 + NaCl\,;\ NH_4Cl + NaNO_3 + NH_4NO_3\,;$$

above the transition point :

$$NaCl + NH_4NO_3 + NaNO_3\,;\ NaCl + NH_4NO_3 + NH_4Cl.$$

From this we see that the two salts NH_4Cl and $NaNO_3$ would be able to exist together with solution below the transition point, but not above it. This transition point has not been determined.

Solubility and Transition Point.—The transition point, we have seen, is the point of intersection of four solubility curves (absence of vapour and constant pressure being assumed), and it has been shown by van't Hoff [1] that at this point the product of the solubilities of the salts of the two salt-pairs is equal. At any other temperature, the salt-pair with the lower solubility product will be the stable salt-pair. Thus, from the solubility values of the single salts at a given tempera. ture, it is possible to state which of the salt-pairs is stable at that temperature.

In the case of the reciprocal salt-pairs, $NaCl + NH_4HCO_3$ and $NaHCO_3 + NH_4Cl$, to be discussed later (p. 290), the solubilities of the four single salts, in gram-molecules per litre, at 0°, are 6·1, 1·5, 0·82, and 5·57 respectively. We have, therefore, $6{\cdot}1 \times 1{\cdot}5\ (= 9{\cdot}15) > 0{\cdot}82 \times 5{\cdot}57\ (= 4{\cdot}57)$. At 0°, therefore, the stable salt-pair is $NaHCO_3 + NH_4Cl$; and the two salts NaCl and NH_4HCO_3 cannot coexist in presence of solution.

In the case of the reciprocal salt-pairs,[2] $Na_2Cl_2 + (NH_4)_2B_4O_7$ and $(NH_4)_2Cl_2 + Na_2B_4O_7$, the salts Na_2Cl_2 and $(NH_4)_2Cl_2$ yield, on complete ionisation, four ions, while the borates yield only three. In calculating the products of concentrations, therefore, the solubility values (in gram-molecules) for the two chlorides must be raised to the fourth power, and those for the borates to the third power.[3] At 0°, we have,

$$C^4_{Na_2Cl_2} \times C^3_{(NH)_4B_4O_7} = 3{\cdot}035^4 \times 0{\cdot}203^3 = 0{\cdot}7098$$
$$C^4_{(NH_4)_2Cl_2} \times C^3_{Na_2B_4O_7} = 2{\cdot}761^4 \times 0{\cdot}0549^3 = 0{\cdot}00962.$$

The stable salt-pair is therefore $NH_4Cl + Na_2B_4O_7$.

[1] Van't Hoff and Reicher, *Z. physikal. Chem.*, 1889, **3**, 482.

[2] The formulæ for sodium chloride and ammonium chloride are doubled in order to express their equivalence with the salts of boric acid. (See Sborgi and Franco, *Gazzetta*, 1921, **51**, II., 1.)

[3] See also Meyerhoffer, *Z. physikal. Chem.*, 1905, **53**, 513.

Formation of Double Salts.—In many cases of four-component systems, the transition point is not a point at which one salt-pair passes into its reciprocal, but one at which a double salt is formed. Thus, at 4·4° Glauber's salt and potassium chloride form glaserite and sodium chloride, according to the equation

$$2Na_2SO_4, 10H_2O + 3KCl = K_3Na(SO_4)_2 + 3NaCl + 20H_2O.$$

Above the transition point, therefore, there would be $K_3Na(SO_4)_2$, NaCl, and KCl; and it may be considered that at a higher temperature the double salt would interact with the potassium chloride according to the equation

$$K_3Na(SO_4)_2 + KCl = 2K_2SO_4 + NaCl,$$

thus giving the reciprocal of the original salt-pair. This point has, however, not been experimentally realised.[1]

Transition Interval.—A double salt, we learned (p. 242), when brought in contact with water at the transition point undergoes partial decomposition with separation of one of the constituent salts; and only after a certain range of temperature (transition interval) has been passed, can a pure saturated solution of the double salt be obtained. A similar behaviour is also found in the case of reciprocal salt-pairs. In the case of each salt-pair there will be a certain range of temperature, called the transition interval, within which, if excess of the salt-pair is brought into contact with water, interaction will occur and one of the salts of the reciprocal salt-pair will be deposited. For the salt-pair which is stable below the transition point, the transition interval will extend down to a certain temperature below the transition point; and for the salt-pair which is stable above the transition point, the transition interval will extend up to a certain temperature above the transition point. Only when the temperature is below the lower limit or above the upper limit of the transition interval, will it be possible to prepare a solution saturated only for the one salt-pair. In the case of ammonium chloride and sodium nitrate the lower limit of the transition interval is 5·5°, so that above this temperature and up to that of the transition point (unknown), ammonium chloride and sodium nitrate in contact with water will give rise to a third salt by double decomposition, in this case to sodium chloride.[2]

Graphic Representation.—For the graphic representation of the isothermal equilibria in systems formed by two reciprocal salt-pairs and water, two methods are employed, one due to Löwenherz and the other due to Jänecke. In these systems, it may be recalled, an isothermal can be represented completely only by a three-dimensional model.

[1] See Meyerhoffer, *Z. physikal. Chem.*, 1899, **28**, 459.

[2] Compare the reciprocal salt-pair NaCl—NH_4HCO_3 (p. 290). In this case the upper limit of the transition interval was found by extrapolation of the solubility curve for $NaHCO_3 + NH_4Cl + NH_4HCO_3$ and $NaHCO_3 + NH_4Cl + NaCl$ to be 32° (Fedotieff, *Z. physikal. Chem.*, 1904, **49**, 179).

A. According to the *method of Löwenherz*,[1] four axes are chosen intersecting at a point like the edges of a regular tetrahedral pyramid (Fig. 146). The four corners of the base of the pyramid represent the pure salts, the members of a particular salt-pair being represented by opposite corners of the square. Thus, if we consider the reciprocal salt-pairs (Na, K)—(NO_3, Cl), we may represent $NaNO_3$ by A, KNO_3 by B, KCl by C, and NaCl by D. Along the four axes, starting from the vertex O, the equivalent molecular amounts of the different salts are measured.

To represent a given system consisting of xB, yC, and zD in a given amount of water (where B, C, and D represent equivalent molecular amounts of the salts), measure off on OB and OC lengths Oc and Ob equal to x and y respectively. From the points b and c lines ba and ca are drawn parallel to OB and OC. The point of intersection a (Fig. 146) then represents a solution containing xB and yC ($ab = x$; $ac = y$). From a a line aP is drawn parallel to OD and equal to z. P then represents the solution of the above composition.

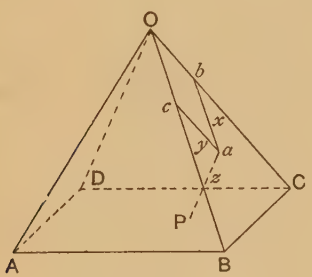

Fig. 146.

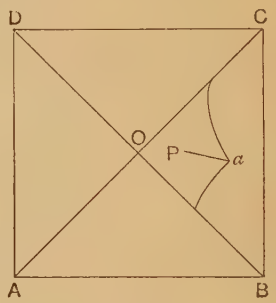

Fig. 147.

It will be understood, from the general method of construction, that the same point, P, will be reached if one first of all measures off on OC and OD lengths equal to y and z respectively, draws from the points so obtained lines parallel to OD and OC respectively, and then, from the point of intersection draws a line of length x, parallel to the edge OB.

In expressing the composition of the quaternary solutions, results of analysis will be grouped so as to contain the stable salt-pair.

It is usual, however, not to employ the three-dimensional figure, but its vertical projection. Fig. 146, if projected orthogonally on the base of the pyramid, would yield a diagram such as is shown in Fig. 147. The projection of the edges of the pyramid form two axes at right angles and give rise to four quadrants similar to those employed for the representation of ternary solutions (p. 240). Here, the point a represents a ternary solution saturated with respect to B and C ; and aP, quaternary solutions in equilibrium with the same two salts as

[1] *Z. physikal. Chem.*, 1894, **13**, 459.

solid phases. Such a diagram represents the conditions of equilibrium only for one definite temperature, and corresponds, therefore, to the isothermal diagrams for ternary systems (p. 240). In such a diagram, since the temperature and pressure are constant (vessels open to the air), a surface will represent a solution in equilibrium with only one solid phase; a line, a solution with two solid phases, and a point, one in equilibrium with three solid phases.

Example.—As an example of the isothermal projection diagram, there may be given one representing the equilibria in the system com-

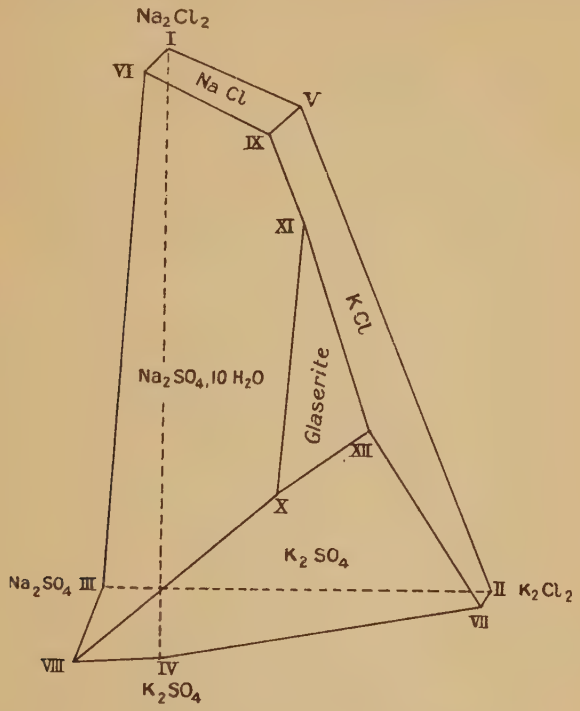

FIG. 148.

posed of water and the reciprocal salt-pair sodium sulphate—potassium chloride for the temperature 0° (Fig. 148).[1] The amounts of the different salts are measured along the four axes, and the composition of the solution is expressed in equivalent gram-molecules per 1000 gram-molecules of water.[2]

The outline of this figure represents four ternary solutions in which

[1] Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

[2] As the quantities of the salts are expressed in *equivalent* gram-molecules, the molecule of sodium and potassium chloride must be doubled in order to be equivalent to sodium sulphate and potassium sulphate.

the component salts have a common acid or basic constituent; viz. sodium chloride –sodium sulphate, sodium sulphate––potassium sulphate, potassium sulphate –potassium chloride, potassium chloride—sodium chloride. These four sets of curves are therefore similar to those discussed in chapter XV. Under particular conditions, the compound glaserite, $K_3Na(SO_4)_2$, is formed. According to van't Hoff and Barschall,[1] glaserite is an isomorphous mixture; but Gossner[2] considers it to be a definite compound having the formula $K_3Na(SO_4)_2$. The composition may, however, vary within certain limits.[3] Point X. gives the composition of the solution saturated for Glauber's salt, potassium sulphate and glaserite; point XI. gives the composition of the solution saturated for Glauber's salt, potassium chloride and glaserite, and point XII. the composition of the solution saturated for potassium sulphate, potassium chloride and glaserite.

The lines which pass inwards from the boundary curves represent solutions containing three salts in contact with only two solid phases; and the points where three lines meet, or where three fields meet, represent solutions in equilibrium with three solid phases, with the phases, namely, belonging to the three concurrent fields.

If it is desired to represent a solution containing the salts, say, in the proportions 51 Na_2Cl_2, 9·5 K_2Cl_2, 3·5 K_2SO_4, the difficulty is met with that two of the salts, sodium chloride and potassium sulphate, lie on opposite axes. To overcome this difficulty, the difference $51 - 3{\cdot}5 = 47{\cdot}5$ is taken and measured off along the sodium chloride axis; and the solution is therefore represented by the point 47·5 Na_2Cl_2, 9·5 K_2Cl_2. In order, therefore, to find the amount of potassium sulphate present from such a diagram, it is necessary to know the total number of salt molecules in the solution. When this is known, it is only necessary to subtract from it the sum of the molecules of sodium and potassium chloride, and the result is equal to twice the number of potassium sulphate molecules. Thus, in the above example, the total number of salt molecules is 64. The number of molecules of sodium and potassium chloride is 57; $64 - 57 = 7$, and therefore the number of potassium sulphate molecules is 3·5.

Another method of representation employed is to indicate the amounts of only two of the salts in a plane diagram, and to measure off the total number of molecules along a vertical axis. In this way a solid model is obtained.

The numerical data from which Fig. 148 was constructed are contained in the table on page 285, which gives the composition of the different solutions at 0°.

From the aspect of these diagrams, the conditions under which the salts can coexist can be read at a glance. Thus, for example, Fig. 148

[1] *Sitz.-Ber. der kgl. preuss. Akad. der Wiss.*, 1903, p. 359; van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, I., p. 34 (Brunswick, 1905); van't Hoff and Barschall, *Z. physikal. Chem.*, 1906, 56, 212.

[2] *Z. Krist.*, 1904, **39**, 155.

[3] Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344; Hamid, *J. Chem. Soc.*, 1926, 199.

shows that at 0° Glauber's salt and potassium chloride can exist together with solution; namely, in contact with solutions having the composition IX. –XI. This temperature must therefore be below the transition point of this salt-pair (p. 279). On raising the temperature to 4·4°, it is found that the curve X.—XI. moves so that the point XI. coincides with point IX.[1] At this point, therefore, there will be *four* concurrent fields, viz. Glauber's salt, potassium chloride, glaserite, and sodium chloride. But these four salts can coexist with solution only at the transition point; so that 4·4° is the transition temperature of the salt-pair: Glauber's salt—potassium chloride. At higher temperatures the lines VIII.—X.—XI. move still further to the left, so that the field for Glauber's salt becomes entirely separated from the field for potassium chloride. This shows that at temperatures above the transition point the salt-pair Glauber's salt—potassium chloride cannot coexist in presence of solution.[2]

Point.	Solid phases.	Composition of solution in gram-mols. per 1000 gram-mols. water.				Total number of salt-molecules.
		Na_2Cl_2.	K_2Cl_2.	Na_2SO_4.	K_2SO_4.	
I.	NaCl	53·84	—	—	—	53·84
II.	KCl	—	34·05	—	—	34·05
III.	Na_2SO_4, $10H_2O$	—	—	5·85	—	5·85
IV.	K_2SO_4	—	—	—	7·47	7·47
V.	NaCl; KCl	48·58	12·75	—	—	61·33
VI.	NaCl; Na_2SO_4,$10H_2O$	53·28	—	2·32	—	55·60
VII.	KCl; K_2SO_4	—	33·66	—	1·25	34·91
VIII.	K_2SO_4; Na_2SO_4,$10H_2O$	—	—	7·99	9·30	17·29
IX.	NaCl; KCl; Na_2SO_4, 10H O	49·44	9·43	—	3·75	62·62
X.	K_2SO_4; Glaserite; Na_2SO_4,$10H_2O$	11·50	16·00	6·0	—	33·50
XI.	KCl; Na_2SO_4,$10H_2O$; Glaserite	41·71	12·15	—	3·35	57·21
XII.	KCl; K_2SO_4; Glaserite	19·41	21·48	2·87	—	43·76

If it is desired to indicate only the mutual relationships of the different components and the conditions for their coexistence (*paragenesis*), a simpler diagram than Fig. 148 can be employed. Thus if the boundary curves of Fig. 148 are drawn so that they cut one another at right angles, a figure such as Fig. 149 is obtained, the Roman numerals here corresponding with those in Fig. 148.

B. The *graphic method of Jänecke and Le Chatelier* [3] possesses the advantage over the method employed by Löwenherz, that the composition of the solutions is expressed not in terms of salts, but in terms

[1] This was determined by Meyerhoffer and Saunders, *Z. physikal. Chem.*, 1899, **28**, 479. The equilibria at 0° determined by these workers, however, do not agree with those obtained by Blasdale. Blasdale did not determine the equilibria at 4·4°.

[2] For the equilibria at higher temperatures, see Blasdale, *J. Ind. Eng. Chem.*, 1918, **10**, 344.

[3] Jänecke, *Z. physikal. Chem.*, 1908, **51**, 132; 1911, **71**, 1; Le Chatelier, *Compt. rend.*, 1894, **118**, 415; 1921, **172**, 345.

of ions, or of acid and basic radicals. Thus the composition of aqueous solutions formed from the salt-pair $M_1S_1 + M_2S_2$ and its reciprocal pair, $M_1S_2 + M_2S_1$, can be represented in accordance with the scheme

$$xM_1, (1 - x)M_2, yS_1, (1 - y)S_2, mH_2O$$

where x, $(1 - x)$, y, $(1 - y)$ are the number of gram-molecules of the ions dissolved in m gram-molecules of water. For the complete representation of the isothermal equilibria a three-dimensional model is required, and as such Jänecke selects a rectangular column on a square base. The four corners of the base represent the pure salts, salts with a common ion being placed at adjacent corners of the square (Fig. 150). The sides AB and CD of the square will represent solutions containing different proportions of M_1 and M_2, and by dividing these sides in the ratio of x to $(1 - x)$, and joining the points a and b so obtained, the line ab will represent quaternary solutions in all of which the ratio of M_1 to M_2 is as x is to $(1 - x)$.

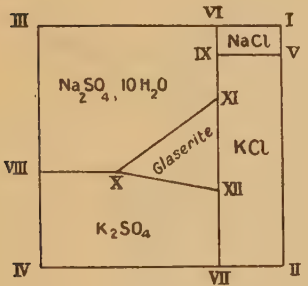

FIG. 149.

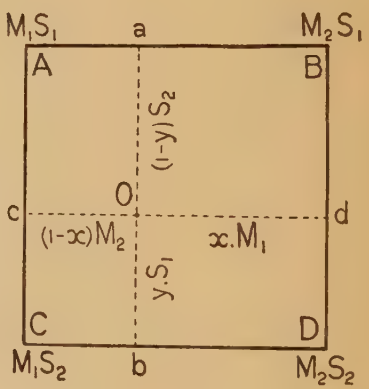

FIG. 150.

Similarly, the line cd represents the composition of solutions in which the radicals S_1 and S_2 are present in the ratio y to $(1 - y)$. The point of intersection O will then, obviously, represent the solution having the composition xM_1, $(1 - x)M_2$, yS_1, $(1 - y)S_2$ dissolved in a given amount of water. To represent the amount of water, a perpendicular is erected at O, and a length corresponding with m gram-molecules is measured off; or better, a length $N = \frac{100\,m}{100 + m}$ (see p. 239). The point in space so obtained represents the solution of the composition

$$xM_1 + (1 - x)M_2 + yS_1 + (1 - y)S_2 + mH_2O.$$

Generally, however, only the plane quadrangular diagram is employed, the relative proportions of the salts only being represented graphically, the amounts of water being indicated, when desired, by numerals.

Conversion Saltpetre.—To illustrate the use of Jänecke's method of representation we may consider briefly the equilibria formed by the reciprocal salt-pairs (Na,K)—(NO_3,Cl) and water, which are of importance for the manufacture of conversion saltpetre, and which have been studied by Uyeda [1] and by Reinders.[2] In this system no compounds or salt hydrates are formed.

In Fig. 151 is shown the projection isothermal for 25°, the faint-drawn lines representing isohydrores or lines of equal water content. At the four corners of the square are the pure salts, the numerals within brackets giving the number of gram-molecules of water in which one

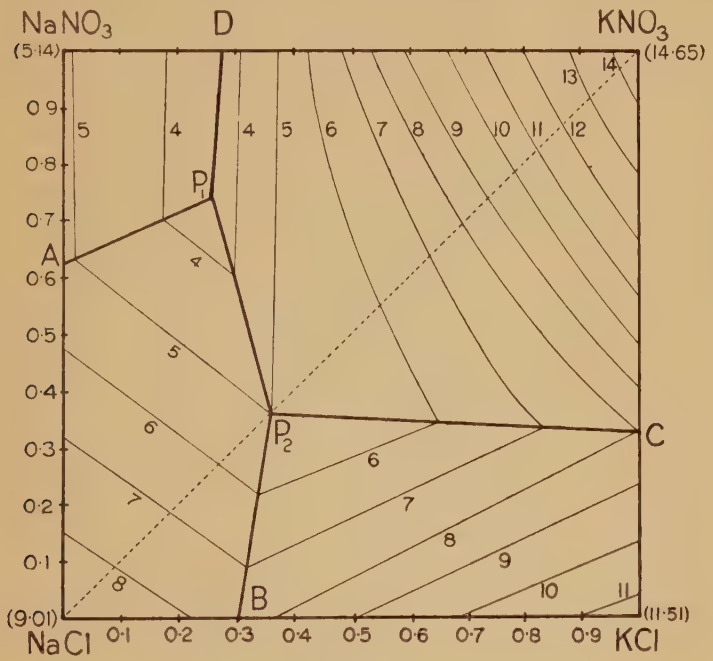

FIG. 151.

gram-molecule of the salt dissolves. At A, we have a solution which is saturated for both $NaNO_3$ and NaCl. Its composition is given by 1·00 Na, 0·624 NO_3, 0·376 Cl, 5·08 H_2O. At B, the solution is in equilibrium with NaCl and KCl as solid phases, and its composition is given by 0·303 K, 0·697 Na, 1·00 Cl, 7·63 H_2O. At C, the solution has the composition represented by 1·00 K, 0·325 NO_3, 0·675 Cl, 8·00 H_2O, and is saturated for KCl and KNO_3; while at D, the solution is in

[1] *Mem. Coll. Sci. Kyoto*, 1909, II., 245.

[2] *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 1065; *Z. anorgan. Chem.*, 1915, **93**, 202.

equilibrium with solid KNO_3 and $NaNO_3$, and has the composition 0·278 K, 0·722 Na, 1·00 NO_3, 3·38 H_2O.

The curves AP_1, DP_1, BP_2, and CP_2 represent the composition of quaternary solutions in equilibrium with two solid salts, and the points P_1 and P_2 solutions in equilibrium with three solid salts. At P_1 the solid phases are NaCl, KNO_3, $NaNO_3$, and the composition of the solution is given by 0·26 K, 0·74 Na, 0·74 NO_3, 0·26 Cl, 3·54 H_2O ; and at P_2 the solid phases are NaCl, KNO_3, KCl, and the solution has the composition 0·36 K, 0·64 Na, 0·36 NO_3, 0·64 Cl, 5·01 H_2O. The curve P_1P_2 gives the quaternary solutions in equilibrium with NaCl and KNO_3.

It will be observed that the fields for NaCl and KNO_3 are adjacent and meet along the curve P_1P_2. These two salts are therefore able to exist together with solution, and are, therefore, at 25°, the stable salt-pair. The fields for $NaNO_3$ and KCl are separated from each other, and the two salts cannot therefore coexist with solution.

The point P_1, which represents a solution saturated for the three solid salts $NaNO_3$, NaCl, KNO_3, lies, as is evident, entirely within the triangular area, all points on which represent solutions the composition of which is expressible in terms of these three salts. P_1, therefore, represents a congruently saturated solution (p. 246). Point P_2, similarly, lies, as is seen, on the diagonal NaCl—KNO_3, and has therefore not passed outside the triangular area for the three salts NaCl, KCl, KNO_3. P_2, therefore, also represents a congruently saturated solution.

As the temperature is raised, however, the position of the points P_1 and P_2 alters, and at temperatures above 50° the point P_2 passes outside the triangular area NaCl, KCl, KNO_3 into the triangular area NaCl, $NaNO_3$, KNO_3. Although the solution, therefore, is in equilibrium with the three salts NaCl, KCl, KNO_3, its composition is not expressible in positive quantities of these salts. Thus, at 100°, the solution saturated for NaCl, KCl KNO_3 has the composition 35·9 grams NaCl, 47·0 grams $NaNO_3$, and 192·2 grams KNO_3 in 100 grams of water. The solution is thus incongruently saturated (p. 246).

In using the Jänecke diagram it may be noted that a solution represented by a point in one of the four areas of Fig. 151 will be in equilibrium with the solid salt belonging to that area. Thus a point in the area to the right of DP_1P_2C will represent the composition of a solution in equilibrium with potassium nitrate as single solid phase. On evaporating such a solution isothermally, potassium nitrate will separate out, and the composition will change in a straight line direction away from the corner of the rectangle, KNO_3, until a point on one of the curves DP_1, P_1P_2, or P_2C is reached. At this point, a second solid phase can begin to separate out.

The solubilities at 5° and 100° are given in the following table.

From the information yielded by the isothermal diagrams based on the solubility data, it is possible to decide the conditions under which potassium nitrate can best be prepared by double decomposition between potassium chloride and sodium nitrate. Thus Reinders has

Temperature.	Solid phases.	Composition of the solution.						
		Grams of salt in 100 grams of water.				xK, $(1-x)$Na, y NO_3, $(1-y)$Cl, m H_2O.		
		NaCl	KCl.	$NaNO_3$.	KNO_3.	x.	y.	m.
5°	$NaNO_3$; KNO_3	—	—	82·10	18·1	0·155	1·00	4·80
	$NaNO_3$; KNO_3; NaCl	29·1	—	44·3	14·0	0·12	0·57	4·80
	NaCl; KCl; KNO_3	38·5	0·64	—	20·7	0·23	0·22	6·50
	NaCl; KCl	31·50	10·40	—	—	0·207	0	8·19
100°	$NaNO_3$; KNO_3	—	—	233·6	218·0	0·44	1·00	1·13
	$NaNO_3$; KNO_3; NaCl	6·5	—	207·5	194·6	0·43	0·975	1·24
	NaCl; KCl; KNO_3	35·9	—	47·0	192·2	0·62	0·80	1·81
	NaCl; KCl	27·3	36·2	—	—	0·51	0	5·83

found that the best yield of potassium nitrate, working between the temperatures 5° and 100°, is obtained in the following manner: 0·80 gram-molecule of sodium nitrate, 0·62 gram-molecule of potassium chloride, and 1·81 gram-molecules of water are mixed together at 100°. There is deposited from the solution 0·42 gram-molecule of sodium chloride, and a mother liquor is produced having the composition 0·38 Na, 0·62 K, 0·20 Cl, 0·80 NO_3, 1·81 H_2O. This solution is saturated for sodium chloride, and also for potassium nitrate and potassium chloride. Its composition corresponds to the point P_2 on the isothermal for 100°, and lies above the dotted line shown in Fig. 151.[1] The mother liquor is separated from the solid sodium chloride and cooled down to 5°. Since, however, at this temperature, the above solution would deposit not only potassium nitrate but also sodium chloride and sodium nitrate, 0·371 gram-molecule of water is added to the solution, so as to give the composition 0·62 K, 0·38 Na, 0·80 NO_3, 0·20 Cl, 2·181 H_2O. From this solution there crystallises out at 5°, 0·563 KNO_3, and a solution is left having the composition 0·057 K, 0·38 Na, 0·24 NO_3, 0·20 Cl, 2·18 H_2O. The cycle is then repeated by heating this solution to 100°, adding a mixture of 0·563 KCl + 0·563 $NaNO_3$ and evaporating off 0·371 H_2O. During the evaporation there separates out 0·563 NaCl. This is removed, the solution is diluted by addition of 0·371 H_2O, and again cooled down to 5°.

During each cycle, $0{\cdot}563 \times 100/0{\cdot}62 = 90{\cdot}8$ per cent. of the potassium chloride is recovered as potassium nitrate; or, from each 100 grams of solution at 100° there are obtained 0·461 gram-molecule = 46·6 grams of potassium nitrate.

General Description of the Method.—Having discussed the process which may be employed for the production of potassium nitrate from potassium chloride and sodium nitrate, a general statement may now be given of the conditions under which one pair of salts

[1] The student should construct the equilibrium diagram from the data given above.

belonging to a reciprocal salt-pair may be most efficiently obtained from the other salt-pair. Calling the salts forming the unstable or incompatible salt-pair the reactants, and the salts forming the stable or compatible salt-pair the resultants, we may state the general conditions for successful and efficient working by a multiple temperature cycle as follows.

To a solution, which is frequently called a *nucleus solution*, and which is used over and over again, equivalent quantities of the reactants are added in such amount as will produce a solution saturated with respect to one resultant only, at the upper limit of temperature used in the process. The mother liquor obtained, after separation of the solid resultant, is cooled down to such a temperature that the quantity of the second resultant deposited is equivalent to the amount of the first resultant removed at the higher temperature. After separation of the second resultant, the mother liquor will have the composition of the original nucleus solution, and the cycle of processes can then be repeated. If, at any stage of the cycle, water has to be added in order to adjust the composition of the solutions, this water is removed at a later stage of the cycle.

A consideration of the above conditions will show that the point in the equilibrium diagram representing saturation with respect to the one resultant, at the *higher* temperature, lies well within the saturation field of the second resultant at the *lower* temperature. From this it follows that an infinite number of nucleus solutions are theoretically possible, but since the object of the manufacturer is to obtain, during each operation, as large an amount of salt as possible per unit of volume of liquor, it usually happens that, for a particular pair of temperatures between which the process is carried out, there is a unique nucleus solution which gives the best results. This solution has almost always a composition such that when the appropriate equivalent amounts [1] of the reactants have been added to it at the higher temperature, and one of the resultants has separated out, a solution is obtained which is represented by a characterised point in the diagram, that is, by a point representing a solution saturated for three solid phases. Thus, in the case of the production of conversion saltpetre, referred to above, the nucleus solution has the composition 0·057 K, 0·38 Na, 0·24 NO_3, 0·20 Cl, 2·18 H_2O. On addition to this solution of a mixture of 0·563 KCl + 0·563 $NaNO_3$ at 100°, and after the evaporation of 0·371 H_2O, a mother liquor is obtained having the composition 0·38 Na, 0·62 K, 0·20 Cl, 0·80 NO_3, 1·81 H_2O. This solution is, as we have seen, saturated for sodium chloride, potassium nitrate, and potassium chloride. During the evaporation, 0·563 NaCl separates out.

Ammonia-Soda Process.—One of the most important applications of the Phase Rule to systems of four components with reciprocal

[1] These are the amounts of the two salts which are deposited during each cycle of the process.

salt-pairs has been made by Fedotieff [1] in his investigations of the conditions for the formation of sodium carbonate by the so-called ammonia-soda (Solvay) process.[2] This process consists, as is well known, in passing carbon dioxide through a solution of common salt saturated with ammonia.

Whatever differences of detail there may be in the process as carried out in different manufactories, the reaction which forms the basis of the process is that represented by the equation [3]

$$NaCl + NH_4HCO_3 = NaHCO_3 + NH_4Cl$$

We are dealing here, therefore, with reciprocal salt-pairs, the behaviour of which has just been discussed in the preceding pages. Since the study of the reaction is rendered more difficult on account of the fact that ammonium bicarbonate in solution, when under atmospheric pressure, undergoes decomposition at temperatures above 15°, this temperature was the one chosen for the detailed investigation of the conditions of equilibrium. Since, further, it has been shown by Bodländer [4] that the bicarbonates possess a definite solubility only when the pressure of carbon dioxide in the solution has a definite value, the measurements were carried out in solutions saturated with this gas. This, however, does not constitute another component, because we have made the restriction that the sum of the partial pressures of carbon dioxide and water vapour is equal to 1 atmosphere. The concentration of the carbon dioxide is, therefore, not independently variable (p. 7).

In order to obtain the data necessary for a discussion of the conditions of soda formation by the ammonia-soda process, solubility determinations with the four salts, NaCl, NH_4Cl, NH_4HCO_3, and $NaHCO_3$ were made, first with the single salts and then with the salts in pairs. The results obtained are represented graphically in Fig. 152,

[1] *Z. physikal. Chem.*, 1904, **49**, 162. See also Toporescu, *Compt. rend.*, 1922, **174**, 870; 1922, **175**, 268; Le Chatelier, *ibid.*, 1922, **174**, 836.

[2] Other commercial processes in the study of which good service is done by the Phase Rule, is the caustification of the alkali salts (G. Bodländer, *Z. Elektrochem.*, 1905, **11**, 186; J. Herold, *ibid.*, 418; Le Blanc and Novotny, *Z. anorgan. Chem.*, 1906, **51**, 181; Fedotieff, *ibid.*, 1913, **82**, 341), the production of borax by the double decomposition between ammonium borate and sodium chloride (Sborgi and Franco, *Gazzetta*, 1921, **51**, II, 1), and the formation of saltpetre from sodium nitrate and potassium carbonate (Kremann and Zitek, *Sitzungsber. Wien. Akad. math.-naturwiss Klasse*, 1909, **118**, II., *b*). The production of calcium nitrate from calcium chloride and sodium nitrate has been worked out by Gilbert (British Patent, 1917, No. 124, 780) and the production of ammonium nitrate from ammonium sulphate and sodium nitrate by Freeth and Cocksedge (British Patent, 1917, No. 126,678; see also *Chem. Met. Eng.*, **20**, 320). For the preparation of ammonium nitrate from ammonium chloride and sodium nitrate, see Mlle. Wurmser, *Compt. rend.*, 1922, **174**, 1466. For the preparation of barium nitrite from barium chloride and sodium nitrite, see Witt and Ludwig, *Ber.*, 1903, **36**, 4384; Meyerhoffer, *ibid.*, 1904, **37**, 261, 1116; Matuschek, *ibid.*, 1907, **40**, 990. The reciprocal salt-pair (Na,Mg)—(Cl,SO_4) has been studied by Takegami (*Mem. Coll. Sci. Kyoto*, 1921, **4**, 317).

[3] According to W. Mason (*Chem. Z.*, 1914, **38**, 513), the reaction which takes place in practice is represented by $2NaCl + (NH_4)_2CO_3 = Na_2CO_3 + 2NH_4Cl$.

[4] *Z. physikal. Chem.*, 1900, **35**, 32.

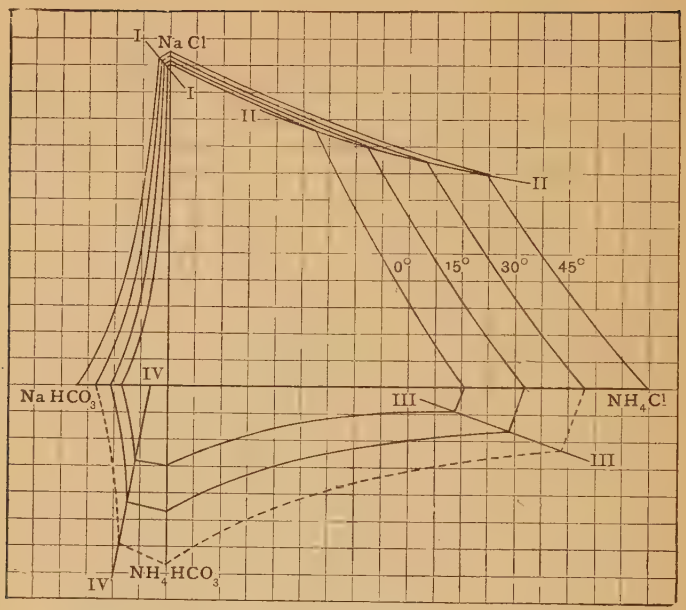

FIG. 152.

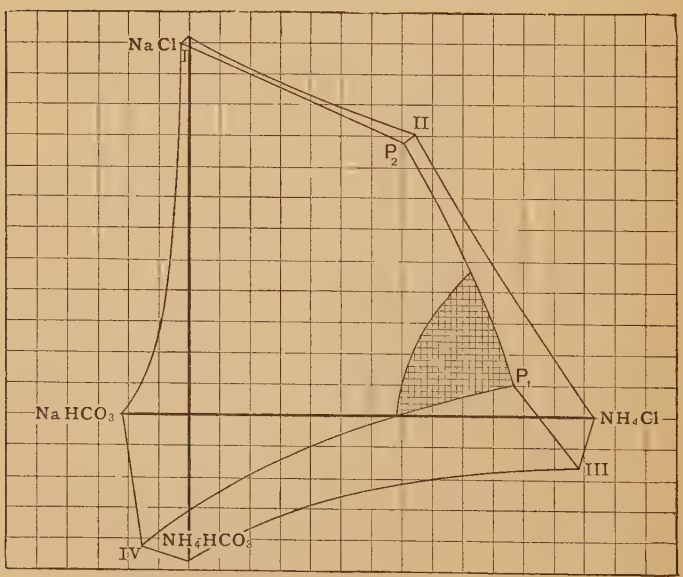

FIG. 153.

which is an isothermal diagram similar to that given in Fig. 148. The points I., II., III., IV. represent the composition of solutions in equilibrium with two solid salts. We have, however, seen (p. 279) that the transition point, when the experiment is carried out under constant pressure (atmospheric pressure), is the point of intersection of four solubility curves, each of which represents the composition of solutions in equilibrium with three salts, viz. one of the reciprocal salt-pairs along with a third salt. Since it was found that the stable salt-pair at temperatures between 0° and 30° is sodium bicarbonate and ammonium chloride, determinations were made of the composition of solutions in equilibrium with $NaHCO_3 + NH_4Cl + NH_4HCO_3$ and with $NaHCO_3 + NH_4Cl + NaCl$ as solid phases. Under the conditions of experiment (temperature = 15°) sodium chloride and ammonium bicarbonate cannot coexist in contact with solution. These determinations gave the data necessary for the construction of the complete isothermal diagram (Fig. 153). For the sake of comparison, the results are also represented in the quadrangular diagram of Jänecke (Fig. 154). The most important of these data are given in the following table (temperature 15°) :—

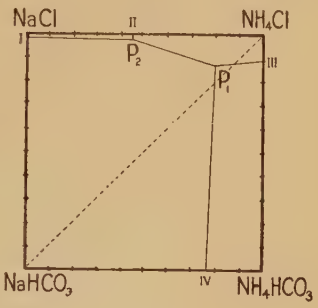

FIG. 154.

Point.	Solid phases.	Composition of the solution in gram-molecules to 1000 grams of water.			
		$NaHCO_3$.	NaCl.	NH_4HCO_3.	NH_4Cl.
—	$NaHCO_3$	1·08	—	—	—
—	NaCl	—	6·12	—	—
—	NH_4HCO_3	—	—	2·36	—
—	NH_4Cl	—	—	—	6·64
I.	$NaHCO_3$; NaCl	0·12	6·06	—	—
II.	NaCl; NH_4Cl	—	4·55	—	3·72
III.	NH_4Cl; NH_4HCO_3	—	—	0·81	6·40
IV.	$NaHCO_3$; NH_4HCO_3	0·71	—	2·16	—
P_1	$NaHCO_3$; NH_4HCO_3; NH_4Cl	0·93	0·51	—	6·28
P_2	$NaHCO_3$; NaCl; NH_4Cl	0·18	4·44	—	3·73

With reference to the solution represented by the point P_1, it may be remarked that it is an incongruently saturated solution (p. 246) ; it lies, as we see from Fig. 154, in the triangular area, the points on which represent solutions the composition of which can be expressed in terms of the three salts $NaHCO_3$, NaCl, NH_4Cl, although the solid phases with which the solution is in equilibrium are $NaHCO_3$, NH_4HCO_3, NH_4Cl. If sodium chloride is added to this solution, the composition

of the latter undergoes change; and if a sufficient amount of the salt is added, the solution P_2 is obtained.

Turning now to the practical application of the data so obtained, consider first what is the influence of concentration on the yield of soda. Since the reaction consists essentially in a double decomposition between sodium chloride and ammonium bicarbonate, then, after the deposition of the sodium bicarbonate, we obtain a solution containing sodium chloride, ammonium chloride, and sodium bicarbonate. In order to ascertain to what extent the sodium chloride has been converted into solid sodium bicarbonate, it is necessary to examine the composition of the solution which is obtained with definite amounts of sodium chloride and ammonium bicarbonate.

Consider, in the first place, the solutions represented by the curve P_2P_1. With the help of this curve we can state the conditions under which a solution, saturated for ammonium chloride, is obtained, after deposition of sodium bicarbonate. In the table below there is given the composition of the solutions which are obtained with different initial amounts of sodium chloride and ammonium bicarbonate. The last two columns give the percentage amount of the sodium used, which is deposited as solid sodium bicarbonate (U_{Na}); and likewise the percentage amount of ammonium bicarbonate which is usefully converted into sodium bicarbonate, that is to say, the amount of the radical HCO_3 deposited (U_{NH_4}):—

Point.	Initial composition of the solutions: grams of salt to 1000 grams of water.		Composition of solutions obtained: gram-equivalents per 1000 grams of water.				U_{Na} per cent.	U_{NH_4} per cent.
	NaCl.	NH_4HCO_3.	HCO_3.	Cl.	Na.	NH_4.		
P_2	479	295	0·18	8·17	4·62	3·73	43·4	95·1
—	448	360	0·31	7·65	3·39	4·56	55·7	93·4
—	417	431	0·51	7·13	2·19	5·45	69·2	90·5
P_1	397	496	0·92	6·79	1·44	6·28	78·8	85·1

This table shows that the greater the excess of sodium chloride, the greater is the percentage utilisation of ammonia (Point P_2); and the more the amount of sodium chloride decreases, the greater is the percentage amount of sodium chloride converted into bicarbonate. In the latter case, however, the percentage utilisation of the ammonium bicarbonate decreases; that is to say, less sodium bicarbonate is deposited, or more of it remains in solution.

Consider, in the same manner, the relations for solutions represented by the curve P_1IV., which gives the composition of solutions saturated with respect to sodium bicarbonate and ammonium bicarbonate. In this case we obtain the following results:—

Point.	Initial composition of the solutions: grams of salt to 1000 grams of water.		Composition of solutions obtained: in gram-equivalents per 1000 grams of water.				U_{Na}.	U_{NH_4}.
	NaCl.	NH_4HCO_3.	HCO_3.	Cl.	Na.	NH_4.		
P_1	397	496	0·92	6·79	1·44	6·28	78·8	85·1
—	351	446	0·99	6·00	1·34	5·65	77·7	82·5
—	316	412	1·07	5·41	1·27	5·21	76·4	79·5
—	294	389	1·12	5·03	1·23	4·92	75·5	75·1
—	234	327	1·30	4·00	1·16	4·14	71·0	68·6

As is evident from this table, diminution in the relative amount of sodium chloride exercises only a slight influence on the utilisation of this salt, but is accompanied by a rapid diminution of the effective transformation of the ammonium bicarbonate. So far as the efficient conversion of the sodium is concerned, we see that it reaches its maximum at the point P_1, and that it decreases both with increase and with decrease of the relative amount of sodium chloride employed; and faster, indeed, in the former than in the latter case. On the other hand, the effective transformation of the ammonium bicarbonate reaches its maximum at the point P_2, and diminishes with increase in the relative amount of ammonium bicarbonate employed. Since sodium chloride is, in comparison with ammonia—even when this is regenerated—a cheap material, it is evidently more advantageous to work with solutions which are relatively rich in sodium chloride (solutions represented by the curve P_1P_2). This fact has also been established empirically.

When, as is the case in industrial practice, we are dealing with solutions which are saturated not for two salts but only for sodium bicarbonate, it is evident that we have then to do with solutions the composition of which is represented by points in the area P_1P_2 I., IV. Since in the commercial manufacture, the aim must be to obtain as complete a utilisation of the materials as possible, the solutions employed industrially must lie in the neighbourhood of the curves P_2P_1 IV., as is indicated by the shaded portion in Fig. 153. The best results, from the manufacturer's standpoint, will be obtained, as already stated, when the composition of the solutions approaches that given by a point on the curve P_2P_1. Considered from the chemical standpoint, the results of the experiments lead to the conclusion that the Solvay process, *i.e.* passage of carbon dioxide through a solution of sodium chloride saturated with ammonia, is not so good as the newer method of Schlösing, which consists in bringing together sodium chloride and ammonium bicarbonate with water.[1]

A modification of the ammonia-soda process in which sodium nitrate or sodium sulphate is used in place of sodium chloride has been sug-

[1] See also Jänecke, *Z. angew. Chem.*, 1907, **20**, 1559.

gested and studied from the point of view of the Phase Rule, by Fedotieff and Koltunoff.[1]

Barium Carbonate and Potassium Sulphate.—As has been found by Meyerhoffer,[2] these two salts form the stable pair, not only at the ordinary temperature, but also at the melting-point. For the ordinary temperatures this was proved in the following manner: A solution with the solid phases K_2SO_4 and $K_2CO_3 . 2H_2O$ in excess can only coexist in contact either with $BaCO_3$ or with $BaSO_4$, since, evidently, in one of the two groups the stable system must be present. Two solutions were prepared, each with excess of $K_2SO_4 + K_2CO_3 . 2H_2O$; and to one was added $BaCO_3$ and to the other $BaSO_4$. After stirring for a few days the barium sulphate was completely transformed to $BaCO_3$, whereas the barium carbonate remained unchanged. Consequently, $BaCO_3 + K_2SO_4 + K_2CO_3 . 2H_2O$ is stable, and, therefore, so also is $BaCO_3 + K_2SO_4$. That $BaCO_3 + K_2SO_4$ is the stable pair also at the melting-point was proved by a special analytical method which allows of the detection of K_2CO_3 in a mixture of the four solid salts. This analysis showed that a mixture of $BaCO_3 + K_2SO_4$, after being fused and allowed to solidify, contains only small amounts of K_2CO_3; and this is due entirely to the fact that $BaCO_3 + K_2SO_4$ on fusion deposits a little $BaSO_4$, thereby giving rise at the same time to the separation of an equivalent amount of K_2CO_3.

Solubility Determinations at 25°.

No.	Solid phases.	100 gms. of the solution contain, in grams, K_2CO_3.	100 gms. of the solution contain, in grams, K_2SO_4.	1000 moles of water contain, in moles, K_2CO_3.	1000 moles of water contain, in moles, K_2SO_4.	Σk_2.	$\frac{K_2CO_3}{K_2SO_4}$.
I.	$K_2CO_3 . 2H_2O + BaCO_3$	53·2	—	147·9	—	—	—
II.	$K_2CO_3 . 2H_2O + K_2SO_4 + BaCO_3$	53·0	0·023	147·8	0·051	—	—
III.	$K_2SO_4 + BaCO_3$	28·5	0·886	52·58	1·296	—	—
IV.		22·1	1·72	37·79	2·333	—	—
V.	$BaCO_3 + K_2SO_4 + BaSO_4$	17·81	2·485	29·11	3·220	32·32	9·03
VI.	$K_2SO_4 + BaSO_4$	12·6	3·92	19·66	4·853	—	—
VII.		5·85	6·76	8·724	7·995	—	—
VIII.	K_2SO_4	—	10·76	—	12·47	—	—
IX.	$BaCO_3 + BaSO_4$	7·35	0·602	10·43	0·676	11·11	15·0
X.		2·85	0·173	3·828	0·184	4·0	21·0

The different solubilities are shown in Fig. 155. In this diagram the solubility of the two barium salts has been neglected. A is the solubility of $K_2CO_3 . 2H_2O$; addition of $BaCO_3$ does not alter this. B is the solubility of $K_2CO_3 . 2H_2O + K_2SO_4 + BaCO_3$. A and B

[1] *Z. anorgan. Chem.*, 1914, **85**, 247; 1923, **103**, 39.

[2] *Z. physikal. Chem.*, 1905, **53**, 513. Compare also, *ibid.*, 1903, **38**, 307. For double decompositions between sparingly soluble lead salts and aqueous solutions of alkali carbonates, see Auerbach and Pick, *Z. Elektrochem.*, 1913, **19**, 827.

almost coincide, since the potassium sulphate is very slightly soluble in the concentrated solution of potassium carbonate. D gives the concentration of the solution in equilibrium with $K_2SO_4 + BaSO_4$. The most interesting point is C. This solution is obtained by adding a small quantity of water to $BaCO_3 + K_2SO_4$, whereupon, being in the transition interval, $BaSO_4$ separates out and an equivalent amount of K_2CO_3 goes into solution. C is the end point of the curve CO, which is called the Guldberg-Waage curve, because these investigators determined several points on it.

In their experiments, Guldberg and Waage found the ratio

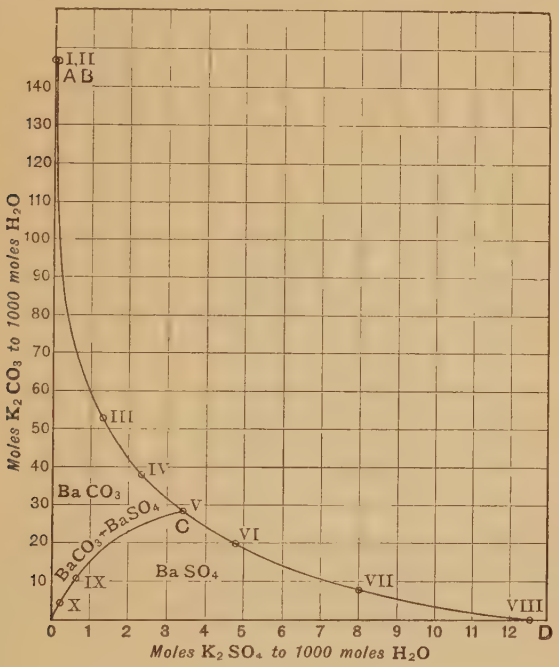

FIG. 155.

$K_2CO_3 : K_2SO_4$ in solution to be constant and equal to 4. This result is, however, not exact, for the curve CO is not a straight line, as it should be if the above ratio were constant, but is concave to the abscissa axis, and more so at lower than at higher temperatures.

The table on page 293 refers to the temperature of 25°. The Roman numerals in the first column refer to the points in Fig. 155. The numbers in the column Σk_2 give the amount, in gram-molecules, of $K_2CO_3 + K_2SO_4$ contained in 1000 gram-molecules of water.

The Guldberg-Waage curve at 100° was also determined, and it was found that the ratio $K_2CO_3 : K_2SO_4$ is also not constant, although the variations are not so great as at 25°.

GULDBERG-WAAGE CURVE AT 100°.

Solid phases.	100 moles of water contain, in moles,		Σk_2.	$\frac{K_2CO_3}{K_2SO_4}$
	K_2CO_3.	K_2SO_4.		
$BaCO_3 + K_2SO_4 + BaSO_4$	23·9	12·65	35·65	1·82
$BaCO_3 + BaSO_4$	6·28	2·02	8·3	3·1
,, ,,	3·17	0·851	4·025	3·7

Oceanic Salts.—The behaviour of reciprocal salt-pairs is of especial importance in connection with the study of the conditions governing the deposition of oceanic salts such as has taken place at Stassfurt. In sea water there are present a number of ions, *e.g.* sodium, potassium, magnesium, calcium, chloride and sulphate ions, which, on evaporation of the water, can give rise to deposits of single salts or double salts in large numbers, the nature of the deposit depending on the concentration of the solution and the temperature of evaporation. To obtain an insight into the conditions under which the different salts can be deposited van't Hoff and his pupils [1] carried out a large number of solubility determinations and investigated the conditions under which the different salts and mixtures of salts exist in equilibrium with solution.

Leaving out of consideration the calcium salts, the relative molecular proportions of the sodium, potassium, and magnesium salts in sea water are expressed by the numbers

100 NaCl, 2·2 KCl, 7·8 $MgCl_2$, 3·8 $MgSO_4$.

The equilibrium conditions for the two salts with a common ion, KCl and $MgCl_2$, have already been discussed (p. 249), and we shall consider briefly here the conditions for equilibrium in the systems formed by the reciprocal salt-pairs (K, Mg) — (Cl, SO_4). Besides the four single salts there exist the double salts carnallite ($KCl . MgCl_2 . 6H_2O$) and schoenite (K_2SO_4, $MgSO_4$, $6H_2O$).

The solubility data for these salt-pairs at 25° are as given in the table on the next page.

These data are represented in Fig. 156 by the graphic method of Löwenherz (p. 282) and van't Hoff (p. 283), and in Fig. 157, by the method of Jänecke (p. 285). These two figures are lettered so as to correspond with each other, and with the data given in the table. In Figs. 156 and 157, the different areas represent solutions

[1] *Untersuchungen über die Bildungsverhältnisse der ozeanischen Salzablagerungen*, edited by Precht and Cohen (Akadem. Verlagsgesellschaft, 1912); van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, Parts I. and II. (Vieweg, 1905 and 1909). A summary of the investigations is given by E. F. Armstrong in the *Reports of the British Association* for 1901, p. 262.

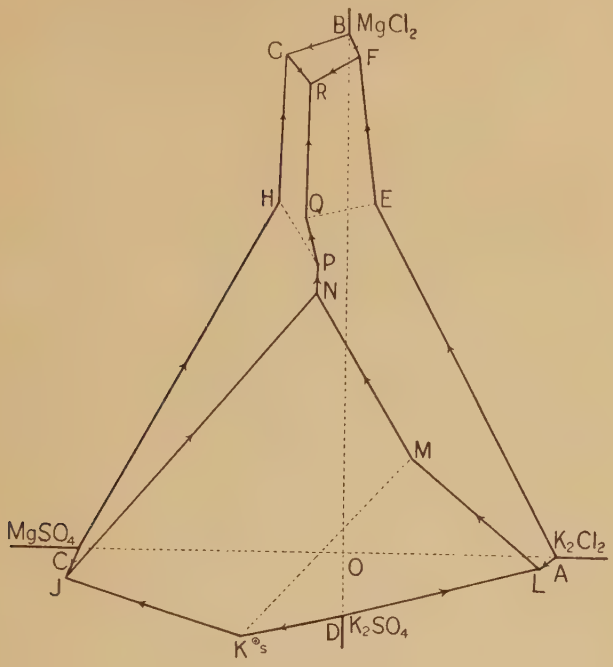

FIG. 156.

Point.	Solid phases.	Moles of salt to 1000 moles of water.			
		K_2Cl_2.	$MgCl_2$.	$MgSO_4$.	K_2SO_4.
A	KCl	44	—	—	—
B	$MgCl_2 . 6H_2O$	—	108	—	—
C	$MgSO_4 . 7H_2O$	—	—	55	—
D	K_2SO_4	—	—	—	12
E	KCl + carnallite	5·5	72·5	—	—
F	$MgCl_2 . 6H_2O$ + carnallite	1	105	—	—
G	$MgCl_2 . 6H_2O + MgSO_4 . 6H_2O$	—	104	14	—
H	$MgSO_4 . 7H_2O + MgSO_4 . 6H_2O$	—	73	15	—
J	$MgSO_4 . 7H_2O$ + schoenite	—	—	58·5	5·5
K	K_2SO_4 + schoenite	—	—	22	16
L	K_2SO_4 + KCl	42	—	—	1·5
M	KCl + K_2SO_4 + schoenite	25	21	11	—
N	KCl + $MgSO_4 . 7H_2O$ + schoenite	9	55	16	—
P	KCl + $MgSO_4 . 7H_2O + MgSO_4 . 6H_2O$	8	62	15	—
Q	KCl + carnallite + $MgSO_4 . 6H_2O$	4·5	70	13·5	—
R	$MgCl_2 . 6H_2O$ + carnallite + $MgSO_4 . 6H_2O$	2	99	12	—

in equilibrium with only one salt, as indicated in the following table :—

Area.	Salt.
ALMNPQE	KCl
EQRF	Carnallite
FRGB	$MgCl_2 . 6H_2O$
GHPQR	$MgSO_4 . 6H_2O$
PHCJN	$MgSO_4 . 7H_2O$
JKMN	Schoenite
LDKM	K_2SO_4

The curves EQ, FR, GR, HP, JN, KM, LM, MN, NP, PQ, QR represent quaternary solutions saturated for two solid salts, namely, for those belonging to the areas adjacent to the curve (*e.g.* curve MN represents quaternary solutions in equilibrium with KCl and schoenite). The dotted curves EQ, HP, and KM represent incongruently saturated solutions.

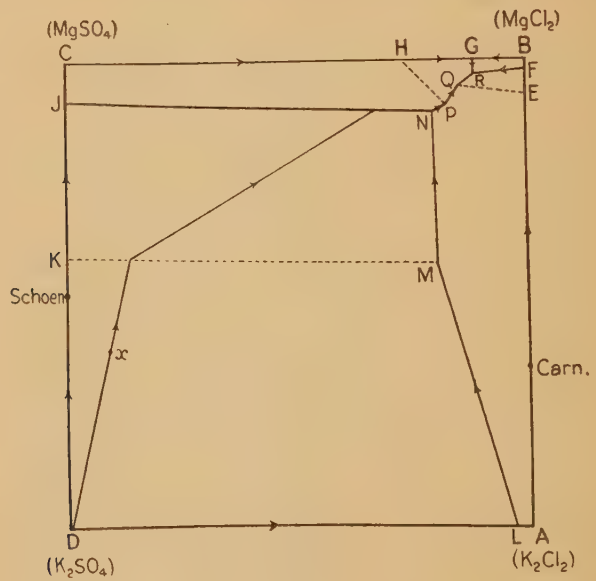

FIG. 157.

Attention may be drawn to the fact that although the solutions corresponding with the points M and N are in equilibrium with three solid salts, of which potassium sulphate or schoenite ($K_2SO_4 . MgSO_4 . 6H_2O$) is one, the composition of the solution is expressed in terms only of KCl, $MgCl_2$, and $MgSO_4$. This shows that the points M and N

represent incongruently saturated solutions (*cf.* p. 246). This is clearly indicated also by the fact that in Fig. 157 the points M and N lie above the diagonal AC, and consequently outside the triangular area for the salts KCl, K_2SO_4 . $MgSO_4$ (*cf.* p. 288).

Crystallisation Paths.—The result of isothermal evaporation of any solution represented by a point in Fig. 156 or Fig. 157 can be ascertained from the diagram. A solution, the composition of which is represented by a point in one of the areas on the diagram, represents a solution saturated with respect to one solid phase, and, on evaporation, the solution will deposit that solid phase. The composition of the solution will then alter away from that of a saturated solution of the solid phase alone; and the change in composition of the solution can be ascertained by joining the point representing the composition of the solid phase[1] with that representing the composition of the original solution, and producing the line. When this line cuts a curve in the equilibrium diagram (Fig. 156 or 157), a second solid phase separates out and the composition of the solution alters accordingly. In the diagrams, the "crystallisation" paths are indicated by arrowheads. In all cases, it is assumed that the salts deposited from solution are removed from time to time or are protected from disappearance.

To take an example, using the diagram, Fig. 157. Suppose a solution represented by the point *x*. This lies in the area for K_2SO_4. A line is therefore drawn from D to *x* and produced. On isothermal evaporation, the composition of the solution will alter along this line, until it reaches a composition represented by the point of intersection of D*x* with KM. At this point schoenite begins to be deposited, and as the solution is incongruently saturated, the potassium sulphate which was first deposited would disappear on continued evaporation. If this potassium sulphate, however, is removed, then schoenite is deposited and the composition of the solution moves across the schoenite area along a path radiating from a point representing the composition of schoenite. This "crystallisation path" cuts the curve JN, and at this point $MgSO_4$. $7H_2O$ begins to separate out. The composition of the solution then alters towards N, at which point potassium chloride is deposited, then to P, when $MgSO_4$. $7H_2O$ passes into $MgSO_4$. $6H_2O$; the crystallisation path then leads to Q, where carnallite separates, and so on to R, where $MgCl_2$. $6H_2O$ is deposited, and the solution dries up to a mixture of $MgSO_4$. $6H_2O$, $MgCl_2$. $6H_2O$ and carnallite. R is the end-point of crystallisation.

With the help of the solubility data given on page 299, it is also possible to follow the crystallisation process in a quantitative manner,[2] and to calculate the amounts of the salts successively deposited on isothermal evaporation. Thus, when a solution containing 1 gram-molecule of potassium sulphate (174·3 grams) and 1 gram-molecule of

[1] In Fig. 156, the point *s* represents the composition of schoenite.
[2] See van't Hoff, *Zur Bildung der ozeanischen Salzablagerungen*, I., p. 26.

magnesium chloride hexahydrate (203·4 grams) was evaporated at 25°, potassium sulphate was first deposited because the above mixture corresponds with a point in the potassium sulphate area. The composition of the solution then alters away from D until schoenite begins to separate out. The potassium sulphate first deposited was not removed from the solution, and so the deposition of schoenite was accompanied by a corresponding disappearance of potassium sulphate, until the point M was reached when potassium chloride just began to be deposited. The evaporation was then discontinued and the amounts of potassium sulphate and of schoenite determined by analysis. The result was 25 grams of K_2SO_4 and 120 grams of $K_2Mg(SO_4)_2 . 6H_2O$. The calculated amounts of these salts can be obtained as follows :—

The composition of the solution at the point M is given by the expression

$$1000\ H_2O + 25\ K_2Cl_2 + 11\ MgSO_4 + 21\ MgCl_2.$$

If, therefore, one starts with a solution $K_2SO_4 + MgCl_2 + aH_2O$, then, on evaporating the solution until point M is reached, a certain amount of potassium sulphate, say, xK_2SO_4, and a certain amount of schoenite, say, $yK_2Mg(SO_4)_2 . 6H_2O$, will have been deposited, and a certain amount of solution of the above composition will remain, say, w(1000 H_2O, 25 K_2Cl_2, 11 $MgSO_4$, 21 $MgCl_2$). Since 1 gram-molecule of chloride (Cl_2) was taken to start with, and since the whole of the chloride radical remains in the residual solution, there must be 1 gram-molecule of chloride in the solution. Since in the expression (1000 H_2O, 25 K_2Cl_2, 11 $MgSO_4$, 21 $MgCl_2$) there are 46 gram-molecules Cl_2, it follows that $w \times 46 = 1$ or $w = \frac{1}{46}$. Similarly, if we consider the amount of the magnesium radical, the original gram-atom of Mg is divided between the solid schoenite and the magnesium salts in the residual solution. We have, therefore, for Mg, $1 = y + 32w$, and, therefore, $y = \frac{7}{23}$. Also, for K_2 we have $1 = x + y + 25w$, and, therefore, $x = \frac{7}{46}$. Consequently, the amount of potassium sulphate deposited is equal to xK_2SO_4, or $\left(\frac{7}{46} \times 174{\cdot}3\right)$ grams = 26·5 grams; and the amount of schoenite deposited will be $yK_2Mg(SO_4)_2 . 6H_2O = \frac{7}{23} \times 402{\cdot}8$ grams, or 122·6 grams. These two amounts, 26·5 grams and 122·6 grams, agree well with the experimentally determined amounts (25 grams and 120 grams respectively), especially when one considers the difficulty of freeing the deposited salts from the mother liquor.

Crystallisation in Presence of Sodium Chloride.—Sea-water, we have seen, contains not only the salts we have just discussed, but also sodium chloride, and consequently, we are dealing not with a

four-component but with a five-component system. The investigation of these systems, however, and the graphic representation of the equilibria are simplified by the fact that owing to the predominance of sodium chloride, deposition of the other salts has always taken place in presence of excess of sodium chloride. In the graphic representation, therefore, we may leave the sodium chloride out of consideration. We obtain, therefore, according to the graphic construction used by van't Hoff, the isothermal model shown in Fig. 158.[1]

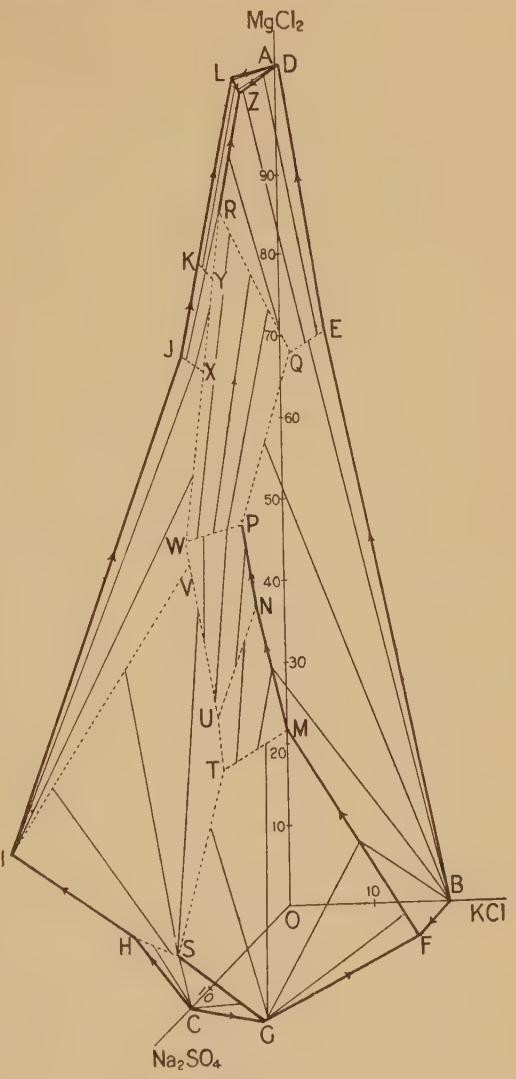

FIG. 158.

In connection with this model it should be mentioned that potassium sulphate does not occur as such, but, in presence of excess of sodium chloride, is deposited as glaserite,

$$K_4Na_2(SO_4)_3.$$[2]

Further, the amount of sodium sulphate, which is given by the expression $Na_2SO_4 = Na_2Cl_2 + MgSO_4 - MgCl_2$, is measured off along the axis OC, which halves the right angle opposite to DOB. At 25° in presence of excess of sodium chloride, sodium sulphate occurs only as anhydrous thenardite.

[1] Jänecke has re-calculated the data obtained by van't Hoff and his co-workers, and has represented them graphically by the method already described. (See *Z. anorgan. Chem.*, 1917, **100**, 161, 176; 1918, **102**, 41; **103**, 1.)

[2] With regard to the nature of glaserite, see p. 284.

Point.	Solutions saturated with NaCl and	Moles of salt to 1000 moles water.				
		Na_2Cl_2.	K_2Cl_2.	$MgCl_2$.	$MgSO_4$.	Na_2SO_4.
O	——	55·5	—	—	—	—
A	$MgCl_2 . 6H_2O$	1	—	106	—	—
B	KCl	44·5	19·5	—	—	—
C	Na_2SO_4	51	—	—	—	12.5
D	$MgCl_2 . 6H_2O$; carnallite	1	0·5	105	—	—
E	KCl; carnallite	2	5·5	70·5	—	—
F	KCl; glaserite	44	20	—	—	4·5
G	Na_2SO_4; glaserite	44	10·5	—	—	14·5
H	Na_2SO_4; astracanite	46	—	—	16·5	3
I	$MgSO_4 . 7H_2O$; astracanite	26	—	7	34	—
J	$MgSO_4 . 7H_2O$; $MgSO_4 . 6H_2O$	4	—	67·5	12	—
K	$MgSO_4 . 6H_2O$; kieserite	2·5	—	79	9·5	—
L	Kieserite; $MgCl_2 . 6H_2O$	1	—	101	5	—
M	KCl; glaserite; schoenite	23	14	21·5	14	—
N	KCl; schoenite; leonite	19·5	14·5	25·5	14·5	—
P	KCl; leonite; kainite	9·5	9·5	47	14·5	—
Q	KCl; kainite; carnallite	2·5	6	68	5	—
R	Carnallite; kainite; kieserite	1	1	85·5	8	—
S	Na_2SO_4; glaserite; astracanite	42	8	—	16	6
T	Glaserite; astracanite; schoenite	27·5	10·5	16·5	18·5	—
U	Leonite; astracanite; schoenite	22	10·5	23	19	—
V	Leonite; astracanite; $MgSO_4 . 7H_2O$	10·5	7·5	42	19	—
W	Leonite; kainite; $MgSO_4 . 7H_2O$	9	7·5	45	19·5	—
X	$MgSO_4 . 6H_2O$; kainite; $MgSO_4 . 7H_2O$	3·5	4	65·5	13	—
Y	$MgSO_4 . 6H_2O$; kainite; kieserite	1·5	2	77	10	—
Z	Carnallite; $MgCl_2 . 6H_2O$; kieserite	1	0·5	100	5	—

The solid phases in the different areas are as under :—

Area.	Solid phase.	Mineralogical name.
ALZD	$MgCl_2 . 6H_2O$	Bischofite
BFMNPQE	KCl	Sylvin
CGSH	Na_2SO_4	Thenardite
DZRQE	$KMgCl_3 . 6H_2O$	Carnallite
FMTSG	$Na_2K_4(SO_4)_3$	Glaserite
SHIVUT	$Na_2Mg(SO_4)_2 . 4H_2O$	Astracanite
JXWVI	$MgSO_4 . 7H_2O$	Reichardtite
JXYK	$MgSO_4 . 6H_2O$	—
KYRZL	$MgSO_4 . H_2O$	Kieserite
TUNM	$K_2Mg(SO_4)_2 . 6H_2O$	Schoenite
NUVWP	$(K, Na)Mg(SO_4)_2 . 4H_2O$	Leonite
PWXYRQ	$KCl . MgSO_4 . 3HO_2$	Kainite

The relations met with here, as can be seen from a glance at the diagram, Fig. 158, are considerably more complex than those found in absence of sodium chloride. The discussion of the simpler systems, however, will enable us to understand the relations shown graphically

in Fig. 158, where also the crystallisation paths are indicated by arrow-heads and the lightly drawn lines radiating from different points in the diagram and crossing the fields for the different solid phases. The experimental data on which the graphic representation is based, are given in the table on page 304.

The equilibria represented in the diagram, Fig. 158, are the stable equilibria. On evaporation of a solution of sea-water, however, super-saturation occurs, in some cases, with great ease, and the stable phase may be entirely missed.

Fig. 158 gives a picture of the relations between the different salts only at 25°. As the temperature is altered the solubility relations also alter; and the areas for the different solid salts change and may entirely disappear, while new salts, represented by new areas in the diagram, make their appearance. Thus schoenite, which at 25° is stable, becomes at 26° unstable, and the schoenite area entirely disappears from the isothermal diagram. The areas for leonite and glaserite then become adjacent, and these two salts can exist in contact with solution. From determinations of the solubilities at a number of different temperatures, a series of paragenetic diagrams (p. 285) can be constructed; and from these and a knowledge of the salts occurring together in the salt-deposits, it is possible to tell the temperature at which deposition of the salts had taken place. The different salt layers, therefore, constitute a "geological thermometer."

Diagrams similar to that shown in Fig. 158 may also be used in order to ascertain the best conditions for obtaining different salts from solution by crystallisation.[1]

[1] See, for example, the discussion of the conditions for obtaining potash and other constituents from sea-water bittern, by Hildebrand, *J. Ind. Eng. Chem.*, 1918, **10**, 96.

APPENDIX.

EXPERIMENTAL DETERMINATION OF THE TRANSITION POINT.

For the purpose of determining the transition temperature, a number of methods have been employed, and the most important of these will be briefly described here. In any given case it is sometimes possible to employ more than one method, but all are not equally suitable, and the values of the transition point obtained by the different methods are not always identical. Indeed, a difference of several degrees in the value found may quite well occur.[1] In each case, therefore, some care must be taken to select the method most suitable for the purpose.

I. The Dilatometric Method.—Since, in the majority of cases, transformation at the transition point is accompanied by an appreciable change of volume, it is only necessary to ascertain the temperature at which this change of volume occurs, in order to determine the transition point. For this purpose the *dilatometer* is employed, an apparatus which consists of a bulb with capillary tube attached, and which constitutes a sort of large thermometer (Fig. 159). Some of the substance to be examined is passed into the bulb A through the tube B, which is then sealed off. The rest of the bulb and a small portion of the capillary tube is then filled with some liquid, which, of course, must be without chemical action on the substance under investigation. A liquid, however, may be employed which dissolves the substance, for, as we have seen (p. 58), the transformation at the transition point is, as a rule, accelerated by the presence of a solvent. On the other hand, the liquid must not dissolve in the substance under examination, for the temperature of transformation would be thereby altered.

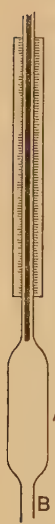

Fig. 159.

In using the dilatometer, two methods of procedure may be followed. According to the first method, the dilatometer containing the form stable at lower temperatures is placed in a thermostat, maintained at a constant temperature, until it has taken the temperature of the bath. The height of the meniscus is then read on a millimetre scale attached to the capillary. The temperature of the thermostat is then raised degree by degree, and the height of the meniscus at each point ascertained. If, now, no change takes place in the solid, the expansion will be practically

[1] See Schwarz, *Beiträge zur Kenntnis der umkehrbaren Umwandlungen polymorpher Körper* (Göttingen, 1892); or, Roozeboom, *Heterogene Gleichgewichte*, I., p. 125. Also Barnes and Cooke, *J. Physical Chem.*, 1902, **6**, 172.

uniform, or the rise in the level of the meniscus per degree of temperature will be practically the same at the different temperatures, as represented diagrammatically by the line AB in Fig. 160. On passing through the transition point, however, there will be a more or less sudden increase in the rise of the meniscus per degree (line BC) if the specific volume of the form stable at higher temperatures is greater than that of the original modification ; thereafter, the expansion will again be uniform (line CD). Similarly, on cooling, contraction will at first be uniform, and then at the transition point there will be a relatively large diminution of volume.

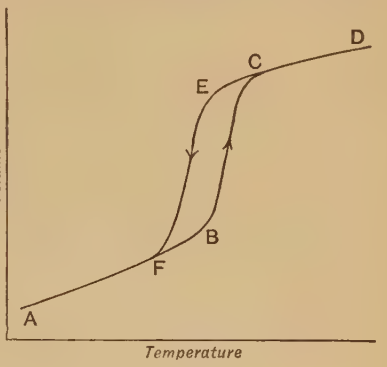

FIG. 160.

If transformation occurred immediately the transition point was reached, the sudden expansion and contraction would take place at the same temperature. It is, however, generally found that there is a lag, and that with rising temperature the relatively large expansion does not take place until a temperature somewhat higher than the transition point ; and with falling temperature the contraction occurs at a temperature somewhat below the transition point. This is represented in Fig. 160 by the lines BC and EF. The amount of lag will vary from case to case, and will also depend on the length of time during which the dilatometer is maintained at constant temperature.

As an example, there may be given the results obtained in the determination of the transition point at which sodium sulphate and magnesium sulphate form astracanite (p. 234).[1] The dilatometer was charged with a mixture of the two sulphates.

Temperature.	Level of oil in capillary.	Rise per 1°.
15·6°	134	7
16·6°	141	7
17·6°	148	6
18·6°	154	7
19·6°	161	7
20·6°	168	73
21·6°	241	2
22·6°	243	8
23·6°	251	8
24·6°	259	—

The transition point, therefore, lies about 21·6° (p. 234).

The second method of manipulation depends on the fact that, while above or below the transition point transformation of one form into the

[1] Van't Hoff and van Deventer, *Z. physikal. Chem.*, 1887, **1**, 173.

other can take place, at the transition point the two forms undergo no change. The bulb of the dilatometer is, therefore, charged with a mixture of the stable and metastable forms and a suitable liquid, and is then immersed in a bath at constant temperature. After the temperature of the bath has been acquired, readings of the height of the meniscus are made from time to time to ascertain whether expansion or contraction occurs. If expansion is found, the temperature of the thermostat is altered until a temperature is obtained at which a gradual contraction takes place. The transition point must then lie between these two temperatures; and by repeating the determinations it will be possible to reduce the difference between the temperatures at which expansion and contraction take place to, say, 1°, and to fix the temperature of the transition point, therefore, to within half a degree. By this method the transition point, for example, of sulphur was found to be 95·6° under a pressure of 4 atm.[1] The following are the figures obtained by Reicher, who used a mixture of 1 part of carbon disulphide (solvent for sulphur) and 5 parts of turpentine as the measuring liquid.

Temperature 95·1°.

Time in minutes.	Level of liquid.
5	343·5
30	340·5
55	335·75
65	333

Temperature 96·1°.

Time in minutes.	Level of liquid.
5	342·75
30	354·75
55	360·5
60	361·5

Temperature 95·6°.

Time in minutes.	Level of liquid.
5	368·75
100	368
110	368·75

At a temperature of 95·1° there is a contraction, *i.e.* monoclinic sulphur passes into the rhombic, the specific volume of the former being greater than that of the latter. At 96·1°, however, there is expansion, showing that at this temperature rhombic sulphur passes into mono-

[1] Reicher, *Z. Kryst.*, 1884, **8**, 593. See also footnote, p. 54.

clinic ; while at 95·6° there is neither expansion nor contraction. This is, therefore, the transition temperature ; and since the dilatometer was sealed up to prevent evaporation of the liquid, the pressure within it was 4 atm.

II. Measurement of the Vapour Pressure.—In the preceding pages it has been pointed out repeatedly that the vapour pressures of the two systems undergoing reciprocal transformation become identical at the transition point (more strictly, at the triple or multiple point), and the latter can therefore be determined by ascertaining the temperature at which this identity of vapour pressure is established. The apparatus usually employed for this purpose is the Bremer-Frowein tensimeter.[1]

This apparatus has the form shown in Fig. 161. It consists of a **U**-tube, the limbs of which are bent close together, and placed in front of a millimetre scale. The bend of the tube is filled with oil or other suitable liquid, *e.g.* bromonaphthalene. If it is desired to measure the dissociation pressure of, say, a salt hydrate, concentrated sulphuric acid is placed in the flask *e*, and a quantity of the hydrate, well dried and powdered,[2] in the bulb *d*. The necks of the bulbs *d* and *e* are then sealed off. Since, as we have learned, suspended transformation may occur, it is advisable first partially to dehydrate the salt, in order to ensure the presence of the second solid product of dissociation ; the value of the dissociation pressure being independent of the degree of dissociation of the hydrate (p. 81). The small bulbs *d* and *e* having been filled, the apparatus is placed on its side, so as to allow the liquid to run from the bend of the tube into the bulbs *a* and *b* ; it is then exhausted through *f* by means of a mercury pump, and sealed off. The apparatus is now placed in a perpendicular position in a thermostat, and kept at constant temperature until equilibrium is established. Since the vapour pressure on the side containing the sulphuric acid may be regarded as zero, the difference in level of the two surfaces of liquid in the **U**-tube gives directly the dissociation pressure of the hydrate in terms of the particular liquid employed ; if the density of the latter is known, the pressure can then be calculated to centimetres of mercury.

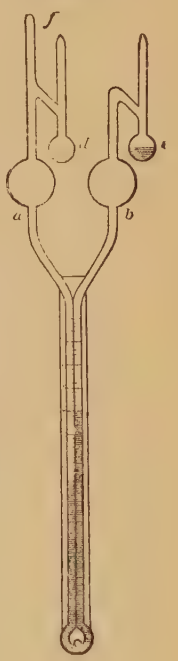

FIG. 161.

In recent years an improved form of tensimeter and method of working, whereby much greater accuracy has been achieved, have been introduced by E. J. Hartung.[3]

Vapour pressures, also, may be determined by a dynamical method,[4]

[1] *Z. physikal. Chem.*, 1887, **1**, 5 ; 1895, **17**, 52. See also Schottky, *ibid.*, 1908, **64**, 415.

[2] It is important to powder the salt, since otherwise the dehydration of the hydrate and the production of equilibrium occurs with comparatively great tardiness.

[3] *Trans. Faraday Soc.*, 1920, **15**, Part III., 150. See also Menzies, *J. Amer. Chem. Soc.*, 1920, **42**, 1952.

[4] Tammann, *Annalen d. Physik*, 1888, **33**, 329 ; Partington, *J. Chem. Soc.*, 1911 **99**, 466 ; Baxter and Lansing, *J. Amer. Chem. Soc.*, 1920, **42**, 419 ; Partington and Huntingford, *J. Chem. Soc.*, 1923, **123**, 160 ; Schumb, *J. Amer. Chem. Soc.*, 1923, **45**, 342 ; Baxter and Cooper, *ibid.*, 1924, **46**, 923 ; Bonnell and Jones, *J. Chem. Soc.*, 1926, 321.

according to which a measured volume of dry air is drawn at constant temperature over the hydrates, and the weight of water vapour taken up by the air is determined. One may also determine the vapour pressure by determining the dew-point of air in contact with the hydrate.[1]

III. Solubility Measurements.—The temperature of the transition point can also be fixed by means of solubility measurements, for at that point the solubility of the two systems becomes identical. Reference has already been made to several cases in which this method was employed, *e.g.* ammonium nitrate (p. 168), Glauber's salt (p. 176), astracanite and sodium and magnesium sulphates (p. 234).

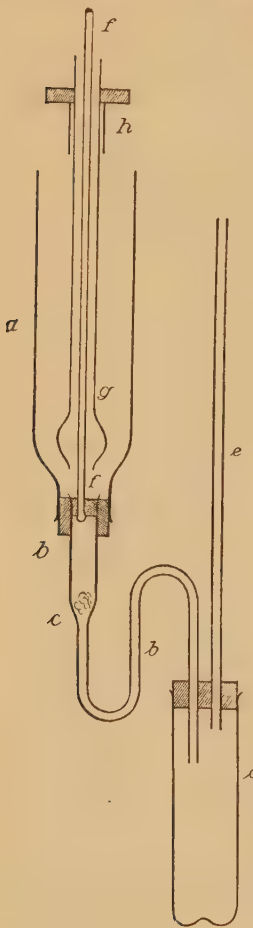

FIG. 162.

The determinations of the solubility can be carried out in various ways. One of the simplest methods, which also gives sufficiently accurate results when the temperature is not high or when the solvent is not very volatile, can be carried out in the following manner. The solid substance is finely powdered (in order to accelerate the process of solution), and placed in sufficient quantity along with the solvent in a tube carefully closed by a glass stopper; the latter is protected by a rubber cap, such as a rubber finger-stall. The tube is then rotated in a thermostat, the temperature of which does not vary more than one or two-tenths of a degree, until saturation is produced. The solution is withdrawn by means of a pipette to which a small glass tube, filled with cotton wool to act as a filter, is attached. The solution is then run into a weighing bottle, and weighed; after which the amount of solid in solution is determined in a suitable manner.[2]

For more accurate determinations of the solubility, especially when the solvent is appreciably volatile at the temperature of experiment, other methods are preferable. In Fig. 162 is shown the apparatus employed by H. Goldschmidt,[3] and used to a considerable extent in the laboratory of van't Hoff. This consists essentially of three parts: *a*, a tube in which the solvent and salt are placed; this is closed at the foot by an india-rubber stopper. Through this stopper there passes the bent tube *cb*, which connects the tube *a* with the weighing-tube *d*. At *c* there is a plug of cotton wool. Tube *e* is open to the air. The wider portion of the tube *cb*, which passes through the rubber stopper in *a*, can be closed by a plug attached to a glass rod *ff*, which passes up through

[1] Cumming, *J. Chem. Soc.*, 1909, **95**, 1772.
[2] See Findlay, *Practical Physical Chemistry* (Longmans).
[3] *Z. physikal. Chem.*, 1895, **17**, 153.

a hollow Witt stirrer, *g*. After being fitted together, the whole apparatus is immersed in the thermostat. After the solution has become saturated, the stopper of the bent tube is raised by means of the rod *ff* and a suction-pump attached to the end of *e*. The solution is thereby drawn into the weighing-tube *d*, the undissolved salt being retained by the plug at *c*. The apparatus is then removed from the thermostat, tube *d* detached and immediately closed by a ground stopper. It is then carefully dried and weighed.

Another form of solubility vessel, due to Meyerhoffer and Saunders, is shown in Fig. 163.[1] This consists of a single tube, and the stirring is effected by means of a glass screw.

The progress of the solution towards saturation can be very well tested by determining the density of the solution from time to time. This is conveniently carried out by means of the pipette shown in Fig.

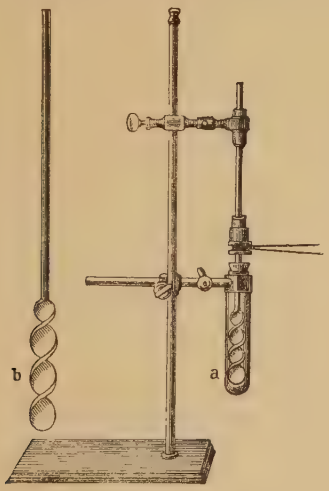

FIG. 163.

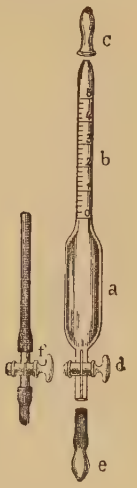

FIG. 164.

164.[2] With this pipette the solution can not only be removed for weighing, but the volume can be determined at the same time. It consists of the wide tube *a*, to which the graduated capillary *b*, furnished with a cap *c*, is attached. To the lower end of the pipette the tube *e*, with plug of cotton wool, can be fixed. After the pipette has been filled by sucking at the end of *b*, the stop-cock *d* is closed and the cap *c* placed on the capillary. The apparatus can then be weighed, and the volume of the solution be ascertained by means of the graduations.

The production of a saturated solution may also, very conveniently, be controlled by means of determinations of the refractive index, using, for example, an Abbé refractometer.[3]

Attention may also be drawn to the apparatus devised by Cohen, de Meester and Moesveld [1] for the accurate determination of solubilities.

[1] *Z. physikal. Chem.*, 1899, **28**, 464.
[2] Meyerhoffer and Saunders, *ibid.*, 1899, **28**, 464.
[3] See Findlay, *Practical Physical Chemistry*.

As has already been insisted, particular care must be paid to the characterisation of the solid in contact with the solution.

IV. Thermometric Method.—If a crystalline solid is heated, its temperature will gradually rise until the melting-point is reached, and the temperature will then remain constant until all the solid has passed into liquid. Similarly, if a substance which can undergo transformation is heated, the temperature will rise until the transition point is reached, and will then remain constant until complete transformation has taken place.

This method, it will be remembered, was employed by Richards for the determination of the transition point of sodium sulphate decahydrate (p. 178). The following figures give the results obtained by Meyerhoffer in the case of the transformation

$$CuK_2Cl_4, 2H_2O \rightleftarrows CuKCl_3 + KCl + 2H_2O,$$

the temperature being noted from minute to minute: 95°, 93°, 91·8°, 91·7°, 92°, 92·3°, 92·4°, 92·2°, 92·2°, 92°, 90·5°, 89°, and then a rapid fall in the temperature. From this we see that the transition point is about 92·2°. It is also evident that a slight supercooling took place (91·7°), owing to a delay in the transformation, but that then the temperature rose to the transition point. This is analogous to the supercooling of a liquid.

A similar halt in the temperature would be observed on passing from lower to higher temperatures; but owing to a lag in the transformation, the same temperature is not always obtained.

V. Optical Method.—The transition point can sometimes be determined by noting the temperature at which some alteration in the appearance of the substance occurs, such as a change of colour or of the crystalline form. Thus, mercuric iodide changes colour from red to yellow, and the blue quadratic crystals of copper calcium acetate change, on passing the transition point, into green rhombs of copper acetate and white needles of calcium acetate (p. 228). Or again, changes in the double refraction of the crystals may be also employed to ascertain the temperature of the transition point. These changes are best observed by means of a microscope.

For the purpose of regulating the temperature of the substance a small copper air-bath is employed.[2]

VI. Electrical Methods.—Electrical methods for the determination of the transition point are of two kinds, based on measurements of conductivity and of electromotive force. Both methods are restricted in their application, but where applicable give very exact results.

The former method, which has been employed in several cases, need not be described here.[3] The second method, however, is of considerable interest and importance, and calls for special reference.

If two pieces, say, of zinc, connected together by a conducting wire, are placed in a solution of a zinc salt, *e.g.* zinc sulphate, the potential of the two electrodes will be the same, and no current will be produced in

[1] *Z. physikal. Chem.*, 1924, **112**, 150.

[2] See Van Eyk, *Z. physikal. Chem.*, 1899, **30**, 446; Hinrichsen and Sachsel, *ibid.*, 1904, **50**, 90.

[3] See, in this connection, Lehfeldt, *Electro-chemistry* (Longmans); and Findlay, *Practical Physical Chemistry* (Longmans). Lucasse and Harris, Jr., *J. Physical Chem.*, 1926, **30**, 930.

the connecting wire. If, however, the zinc electrodes are immersed in two solutions of *different* concentration contained in separate vessels, but placed in connection with each other by means of a bent tube filled with a conducting solution, the potentials at the electrodes will no longer be the same, and a current will now flow through the connecting wire. The direction of this current *in the cell* will be from the weaker to the more concentrated solution.

The greater the difference in the concentration of the solutions with respect to zinc ions, the greater will be the difference of the potential at the two electrodes, or the greater will be the E.M.F. of the cell. When the concentration of the two solutions becomes the same, the E.M.F. will become zero, and no current will pass.

It will now be understood how this method can be made use of for determining the transition point of a salt, when we bear in mind that at the transition point the solubility of the two forms becomes identical. Thus, for example, the transition point of zinc sulphate heptahydrate into hexahydrate could be determined in the following manner. Tube A (Fig. 165) contains, say, a saturated solution of the heptahydrate along with some of the solid salt; tube B, a saturated solution of the hexahydrate along with the solid salt. The tube C is a connecting tube bent downwards so as to prevent the mixing of the solutions by convection currents. ZZ are two zinc electrodes immersed in the solution; the cell is placed in a thermostat and the zinc electrodes connected with a galvanometer. Since at temperatures below the transition point the solubility of the hexahydrate (the metastable form) is greater than that of the heptahydrate, a current will be produced, flowing in the cell from heptahydrate to hexahydrate. As the temperature is raised towards the transition point, the solubilities of the two hydrates also approach, and the current produced will therefore become weaker, because the E.M.F. of the cell becomes less; and when the transition point is attained, the E.M.F. becomes zero, and the current ceases. If the temperature is raised above this, the solubility of the heptahydrate becomes greater than that of the hexahydrate, and a current will again be produced, but in the opposite direction. By noting the temperature, therefore, at which the current ceases, or the E.M.F. becomes zero, the transition temperature can be ascertained.[1]

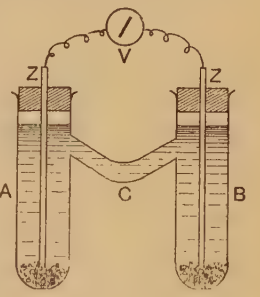

FIG. 165.

In the case just described, the electrodes consisted of the same metal as was contained in the salt. But in some cases, *e.g.* sodium sulphate, electrodes of the metal contained in the salt cannot be employed. Nevertheless, the above electrical method can be used even in those cases, if a suitable non-polarisable mercury electrode is employed.[2]

Although no current is produced when two pieces of zinc are immersed in the same solution of zinc salt, a current will be obtained if two different metals, or even two different modifications of the same

[1] Barnes and Cooke, *J. Physical Chem.*, 1902, **6**, 172.

[2] For a description and explanation of these, the reader should consult the volume in this series by Lehfeldt on *Electro-chemistry*; and van't Hoff, *Bildung und Spaltung von Doppelsalzen*, p. 48 ff.

metal, are employed. Thus an E.M.F. will be established when electrodes of grey and of white tin are immersed in the same solution of tin salt (ammonium stannic chloride), but at the transition point this E.M.F. will become zero. By this method Cohen determined the transition point of grey and white tin (p. 58).

VII. Viscosity Method.—The transition temperatures of a number of salts have also been determined by plotting the viscosities (or times of outflow of a given volume through a capillary) of solutions saturated at different temperatures below and above the transition point.[1] Curves are thus obtained which intersect at the transition point.

[1] Dunstan and Langton *J. Chem. Soc.*, 1912, **101**, 418.

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